THE CATALYTIC VAPOR PHASE OXIDATION OF PINENE TO MALEIC ANHYDRIDE

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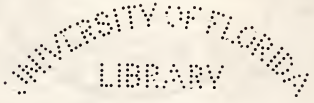

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Introduction

The principal chemical species present in American turpentine, namely pinene and nopinene, or alpha and beta pinene respectively, are complex compounds and are very reactive. Consequently, in planning a research program with the object of creating new industrial outlets for these materials, the greatest opportunity would seem to lie in the direction of new compounds produced by subjecting the turpentine constituents to some of the many reactions to which they are susceptible. It was with this thought in mind that the investigation discussed in this dissertation was undertaken.

A perusal of the literature of terpenes in general and of pinene in particular reveals the fact that these substances undergo oxidation very readily, and that numerous compounds can be made in this way. It is further to be noted that while a large number of investigations have been reported on the action of the usual laboratory oxidizing agents, very little information is available on the action of air on the vapors of terpenes in the presence of oxidation catalysts. For this reason, and in view of the fact that catalytic vapor phase oxidation lends itself readily to continuous plant operation, it was considered of value to investigate this reaction. Pinene was selected as the material to be investigated, first because more valuable information can be obtained from the study of a pure compound than from the study of a complex mixture like commercial turpentine, and secondly because pinene is the major constituent of gum turpentine (1).

THE MECHANISM OF HYDROCARBON OXIDATION

Most of the attempts which have been made to elucidate the mechanism of hydrocarbon oxidation have been concerned with uncatalyzed gas phase reactions, especially in connection with the combustion of fuel in gas engine cylinders, and hence the results do not apply rigorously in the present instance. However, the results of such investigations and the theories which have been advanced to explain them are pertinent to a general understanding of the subject, and therefore will be presented briefly.

The four principal theories which have been advanced to explain the way in which hydrocarbons burn are:

1. The Preferential Combustion of Hydrogen.-Until about 1892 it was generally believed that hydrogen is the most combustible part of a hydrocarbon, and that when the hydrocarbon burns the hydrogen is stripped from the carbon skeleton to form water, leaving free carbon which subsequently burns to carbon monoxide and carbon dioxide. The obvious fact of the formation of soot in the burning of hydrocarbons, especially in the absence of sufficient oxygen for complete combustion, naturally led to such a theory.

2. The Preferential Combustion of Carbon.-The older concept of the preferential combustion of hydrogen had to be abandonned when in 1892 Dixon (2) found that detonation of a mixture of equal volumes of ethylene and oxygen yielded almost exactly the amount of hydrogen and carbon monoxide demanded by the equation

$$C_2H_4 + O_2 = 2H_2 + CO.$$

This and other similar observations led to the belief that carbon is burned first, liberating hydrogen which then burns to water. This theory received additional support when Smithels and Ingle (3) found that hydrogen is present in the inner parts of hydrocarbon flames.

5. Hydroxylation Theory.-Subsequent research has shown that neither of the preferential combustion theories explains all the facts. Principally as a result of the researches of Bone (4) and of Blair and Wheeler (5), the view now is widely held that combustion of hydrocarbons proceeds through an initial combination of oxygen with the hydrocarbon, giving rise to an oxygenated compound, generally an alcohol. The following mechanisms are postulated.

Ethane:

$$CH_3\text{-}CH_3 \longrightarrow CH_3CH_2OH \longrightarrow CH_3CH(OH)_2 \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO \longrightarrow CH_2O + CO + H_2$$

$$CH_2O \longrightarrow HCOOH \longrightarrow OC(OH)_2 \longrightarrow CO_2 + H_2O$$

Long Chains:

$$RCH_2CH_3 \longrightarrow RCH_2CH_2OH \longrightarrow RCH_2CH(OH)_2 \longrightarrow RCH_2CHO + H_2O$$

$$RCH_2CHO \longrightarrow RCH(OH)CHO \longrightarrow RCHO + HCHO \longrightarrow RCHO + H_2 + CO \text{ etc.}$$

Olefins:

$$CH_2{=}CH_2 \longrightarrow CH_2{=}CH(OH) \longrightarrow (HO)HC{=}CH(OH)$$

$$(HO)CH{=}CH(OH) \longrightarrow 2HCHO \longrightarrow H_2 + CO$$

$$2HCHO \longrightarrow H_2O + CO_2$$

$$(HO)CH{=}CH(OH) \longrightarrow HOC\text{-}CHO + H_2 \longrightarrow (COOH)_2 \longrightarrow CO + CO_2 + H_2O \text{ etc.}$$

One objection to the hydroxylation theory is the fact that molecular oxygen contains two oxygen atoms, while only one is required for the introduction of an hydroxyl group into an hydrocarbon molecule. Consequently, for this reaction to occur the oxygen molecule must be previously split into its constituent atoms, a process requiring a very high energy level. Also, if sufficient activation energy were provided to produce atomic oxygen,

the alcohol formed by interaction of this with the hydrocarbon would stand only a remote chance of survival, It would be either immediately decomposed or oxidized to aldehyde. As a matter of fact, aldehydes generally predominate in the product, even when it can be shown that alcohols are formed. For this reason Bone (6) suggested the alternate mechanism:

$$CH_4 + O_2 \longrightarrow CH_2(OH)_2 \longrightarrow HCHO + H_2O \longrightarrow H_2 + CO + H_2O,$$

and explained the formation of alcohols by the interaction of the aldehyde and hydrogen. There is, however, no direct evidence upon which to base a choice between these two very similar mechanisms.

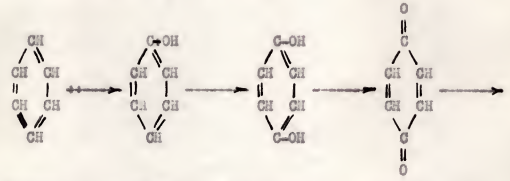
These objections need not apply to catalyzed reactions, however, since in this case the hydrocarbon may not react with molecular oxygen but may react with a catalyst molecule. The usual catalysts are oxides capable of existing in several states of oxidation, and they are therefore readily regenerated by combination with molecular oxygen. The catalyst thus serves as an oxygen "carrier" . Such a mechanism has been proposed by Lucas (7) for the oxidation of benzene by air in the presence of nitrogen oxides. This reaction undoubtedly proceeds through an hydroxylation mechanism, since yields of phenol as high as 50% were obtained, and in addition most of the intermediate compounds demanded by the hydroxylation reaction have been detected in the product.

According to Lucas (7) NO_2 is known to be activated by radiation over a wide range of frequencies, and at the temperature employed in the oxidation of benzene (700 °C.) such activation may occur. The sequence of reactions is:

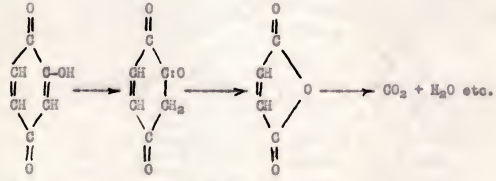
$$NO_2 + E = NO^{\times}_2, \quad (\text{indicates an activated molecule.})$$

$$C_6H_6 + NO_2^{\times} \longrightarrow C_6H_5OH + NO.$$

The nitric oxide then combines with the oxygen present, and the process is repeated. The complete scheme for the oxidation of benzene under these conditions is believed to be as follows:



Benzene Phenol Hydroquinone Quinone

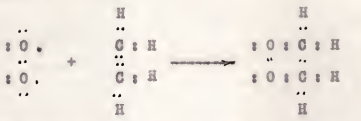


(Enol) (Keto) Maleic Anhydride

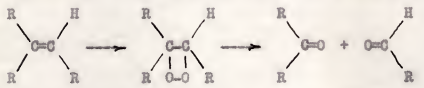
The fact that phenol, hydroquinone, quinone and maleic anhydride have been found in the product of this reaction is convincing evidence of the correctness of the proposed mechanism. Formaldehyde also was detected.

4. Peroxide Theory.-As the result of more recent work, especially on olefin oxidation, the peroxide theory has been developed (8). This theory stems from the rather well-established fact that the oxygen molecule contains two odd or unpaired electrons, and hence should be able readily to

attach itself to any system, such as an ethylenic linkage, which is able to share the unpaired electrons:



The peroxides so formed may decompose to give aldehydes and ketones:



This mechanism will not account for the large amounts of acetaldehyde which can be formed by oxidizing ethylene. However, it is known that ethylene polymerizes at the temperature used in the oxidation, and it may be that the acetaldehyde is derived from the polymerization product. Hence this is not a serious objection to the theory.

To summarize, it may be stated that both the hydroxylation theory and the peroxide theory may be correct under proper conditions, and that no one mechanism can be postulated which is valid under all circumstances. It seems to be fairly well established that the hydroxylation reaction occurs in the oxidation of saturated and aromatic hydrocarbons, while the oxidation of unsaturated systems proceeds through the formation of peroxides.

THE VAPOR PHASE OXIDATION OF TYPICAL HYDROCARBONS

1. Paraffins.--Tremendous quantities of the lower paraffins are available as by-products of the petroleum industry, and consequently considerable research has been carried out with the object of producing oxygenated compounds by direct oxidation of these substances. Such efforts, however, have not been attended with success, and to date no workable process has been developed for the production of pure compounds by the oxidation of paraffins (9). The basic reason for this lack of success is the chemical inertness of the paraffins and their consequent resistance to the primary step in the oxidation process, namely the introduction of an atom of oxygen. This step requires such a high temperature level that once oxidation starts it proceeds through all the intermediate stages, resulting in complete combustion of a large part of the hydrocarbon. Furthermore, the reaction appears to occur homogeneously in the gas phase and therefore to be unaffected by the numerous catalysts so far tried.

2. Olefins.--Because of the fact that olefins react readily with a variety of reagents, such as aqueous and alcoholic acids, hydrogen chloride, chlorine, etc., most of the researches on their utilization as raw materials for organic syntheses have been concerned with such reactions, and little attention has been given to their utilization through direct oxidation. Bone and Wheeler (10), Wilstätter and Bommer (11), Phillips (12), Blair and Wheeler (13), and others have shown that aldehydes can be formed in this way, but no attempts at practical application have been made.

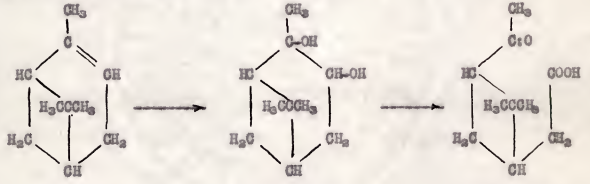
3. Aromatics.—By far the most successful applications of catalytic vapor phase hydrocarbon oxidation have been achieved with aromatic compounds, using various oxides as catalysts. Thus Weiss and Downs (14) report a yield of 60 pounds of maleic anhydride per 100 pounds of benzene when the latter is passed over a catalyst containing vanadium pentoxide. Likewise Gibbs (15), who is credited with the pioneer work in this field, reports a yield of 80% in the commercial production of phthalic anhydride from naphthalene, using the same catalyst. By oxidizing toluene in the same manner it is possible to obtain good yields of either benzaldehyde or benzoic acid by suitable regulation of conditions.(16). Similarly, in the oxidation of anthracene, anthraquinone is readily produced (17). All of these processes are in successful technical operation, and constitute the principal commercial sources of the products named.

4. Terpenes.—In the terpene group virtually no attempts have been made to apply direct catalytic vapor phase oxidation. One broad patent issued to Wedge (18), and dealing primarily with the oxidation of aromatic compounds with ozone in the presence of oxygen-adsorbing catalysts, such as platinum black, platinized asbestos, etc., also claims the oxidation of turpentine by the same process. Schrauth (19) has patented the conversion of turpentine to maleic acid by passing the vapor mixed with air over a catalyst at elevated temperature. This patent is discussed in detail in the section dealing with the action of air on pinene.

THE ACTION OF OXIDIZING AGENTS ON PINENE

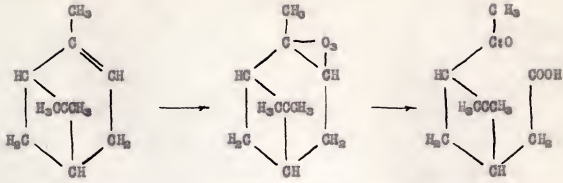
In general, the ordinary laboratory oxidising agents attack pinene either at the double bond with the formation of a glycol or an epoxy compound, or at the carbon atoms adjacent to the double bond with the formation of aldehydes, ketones and alcohols as primary products. Further action of the reagent results in ring fission and the formation first of monocyclic compounds and finally of open chain structures. The following are typical examples.

1. Potassium Permanganate.— This reagent attacks at the double bond through an hydroxylation mechanism. Wallach (20), by using 1% alkaline permanganate at 0° C. was able to prepare pinene glycol. Later Baeyer (21) succeeded in isolating pinonic acid from the products of this reaction. This compound played an important role in the development of the structure of pinene. The reaction proceeds as follows:



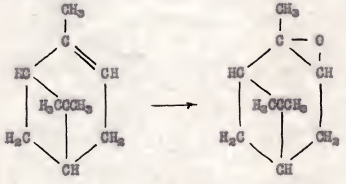
Pinene — Pinene Glycol — Pinonic Acid

2. Ozone.—The primary action of ozone is addition at the double bond, to form an ozonide. This when hydrolyzed gives pinonic acid, as shown in the following scheme (22).



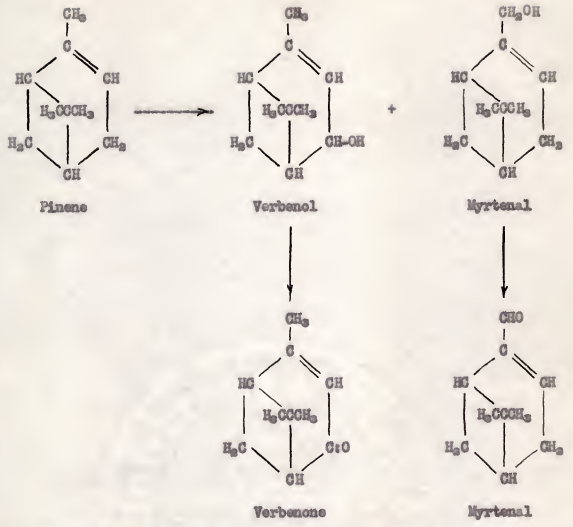
Pinene Pinene Ozonide Pinonic Acid

5. Peroxides.—Hydrogen peroxide, acetyl hydroperoxide, benzoyl hydroperoxide and similar substances generally form the epoxy compound as the first step, in the oxidation process. With acetyl hydroperoxide as reagent pinene oxide can be obtained in 80% yield. The reaction is as follows (25).



Pinene Pinene Oxide

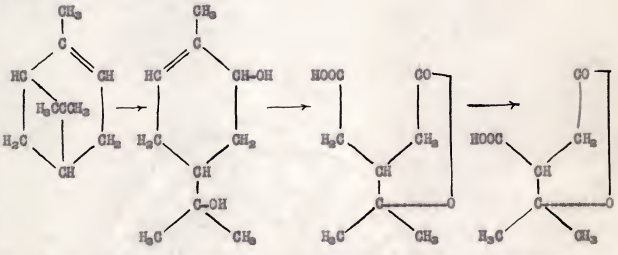
4. Nitrogen Dioxide.—This reagent falls inthe class of substances which attack not at the double bond but at the adjacent carbon atoms. The initial step appears to consist of hydroxylation at these points, followed by oxidation of the alcohols so formed. Thus, with excess pinene the product contains mainly verbenol and myrtenol, while with excess N_2O_4 the corresponding carbonyl compounds verbenone and myrtenal are obtained. Pinocarveol and pinocarvone also are reported as products of this reaction, but it seems probable that these were derived from nopinene which probably was present in the pinene used. The reaction proceeds as follows (24).



5. Selenium Dioxide.--This reagent is a comparatively recent addition to the list of oxidizing agents, and is unique in that it appears quite generally to hydroxylate the carbon atoms adjacent to double bonds, carbonyl groups etc. (25). Its action on pinene therefore is quite similar to that outlined for H_2O_2, the principal products being myrtenol, verbenol, myrtenal, and verbenone (26).

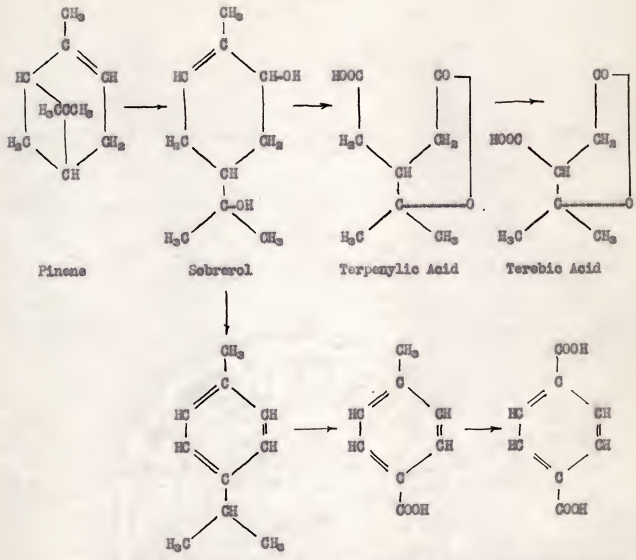
6. Chromic Oxide.--The products obtained by the action of this reagent depend upon the vigor with which it is allowed to react. Mild oxidation results in hydroxylation at the ring carbons alpha to the double bond, with

the formation of verbenol and verbenone as principal products (27). More vigorous oxidation leads to the formation of terpenylic and terebic acids, substances which were important in the determination of the structure of a number of terpenes (28). This indicates that sobrerol, formed by hydration and oxidation, may be the primary product. The reaction is represented by the following equation:



Pinene Sobrerol Terpenylic Acid Terebic Acid

7. Nitric Acid.—The action of this reagent is similar to that of CrO_3, except that dehydration of the sobrerol occurs with the formation of p-cymene. Oxidation of the latter is the probable source of the toluic and terephthalic acids found in the product.(29). The reaction is shown on page 13.



8. Electrolytic Oxidation.--Pinene was oxidized electrolytically by Fichter and Schetty (30). However, they electrolyzed in acid solution, and it is probable that some of their products were formed as a result of the isomerizing and hydrating action of the acid. They found 1,8-terpin, 1,8-cineole, terpineol, dipentene, cymene, terebic acid and formic acid in the product. The first four substances probably were formed by the action of the acid, while the remainder were due to the electrolysis.

THE ACTION OF HEAT ON PINENE

As will be seen later, the temperatures at which vapor phase catalytic oxidation is carried out are well within the range in which pinene undergoes a complicated series of changes. A knowledge of the products of such changes is pertinent to the subject under consideration, and for this reason the behavior of pinene at elevated temperatures now will be discussed.

The action of heat on turpentine and pure pinene has been studied by a number of investigators (31). Gay-Lussac and Lariviere (32) in 1841 found that pyrolysis of turpentine yielded some oils that were more volatile and others less volatile than turpentine. Later Berthelot (33) found that polymerization and other changes took place when turpentine was heated in a sealed tube for ten hours at 250° C. Further investigation by Berthelot (34), Scheil (35), Mokiewski (36), Tilden (37), Schultz (38), Wallach (39), and others, indicated that in general when moderate temperatures are employed, i. e. 300° - 400° C., the products of pyrolysis consist largely of monocyclic terpenes, dipentene predominating, while at higher temperatures, i. e. 600° - 800° C., considerable amounts of aromatics, including benzene, toluene, xylene, p-cymene and naphthalene are formed together with hydrogen, ethylene, isoprene, trimethylethylene and other olefins. As a result of interest in synthetic rubber around 1900, many attempts were made to pyrolize pinene under such conditions that isoprene would be the principal product, but the results were not promising.(40).

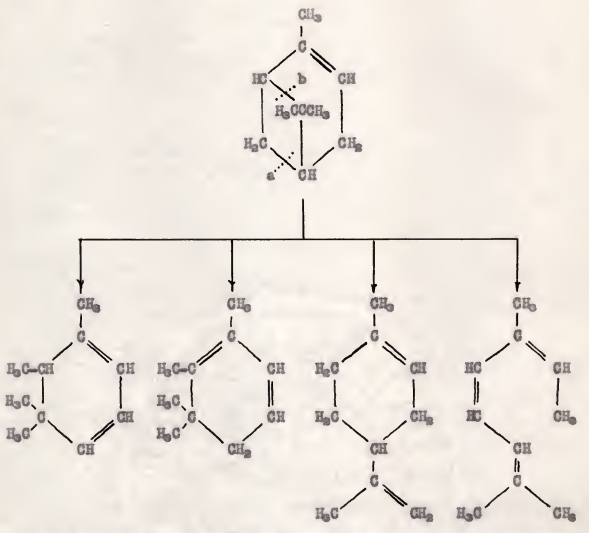
Kinetic studies of the "isomerization" of pinene have been made by Smith (41), Conant and Carlson (42), Kassel (43), and Thurber and Johnson (44).

The most significant work on the pyrolysis of pinene has been done by Arbuzov (45) and by Dupont and Dulou (46). Arbuzov passed pinene over various catalysts at a series of temperatures, and concluded from his results that temperature and not the catalyst is the governing factor. He found unchanged pinene, dipentene, other unidentified monocyclic terpenes, and an aliphatic terpene in the reaction product. The aliphatic terpene later was shown by Arbuzov (47) and by Dupont and Dulou (48) to be allo-ocimene. The results of Arbuzov are summarized in Table I.

Table I. Products of the Pyrolysis of Pinene.

Temperature °C.	Unchanged Pinene %	Allo-Ocimene %	Dipentene %	Other Monocyclics %
360	60	20	—	—
375	23	21	42	—
410	20	20	23	30

Dupont and Dulou (48) identified two new monocyclic terpenes in the product obtained by passing pinene vapor over copper gauze at 300° - 325° C. These workers concluded that pinene may cleave in three ways, as shown in the scheme on page 16. Cleavage at (a) yields alpha and beta pyronene; cleavage at (b) yields dipentene; cleavage at both points yields allo-ocimene.


Alpha Pyronene
Beta Pyronene
Dipentene
Allo-ocimene

THE ACTION OF AIR ON PINENE

The action of air on liquid pinene, a process generally referred to as "autoxidation", was investigated at a very early date. Many years ago it was noted that perfectly dry turpentine when left in contact with air gradually became viscous and drops of water appeared (49). The first product of this reaction to be recognized was sobrerol, a compound which was first obtained pure by Margueron in 1787 (50), although he confused it with terpin hydrate. The compound was characterized by Sobrero (51), for whom it is named. Later Kinzett (52) identified formic, acetic and camphoric acids in the reaction product.

The first systematic investigation was carried out by Schönbein (55), who postulated the initial step as the addition of oxygen. Later Engler (54) showed that pinene oxide is formed, and that the reaction proceeds slowly at 0° C., increases in velocity up to 100° C., and finally decreases above this temperature. He found that the oxide begins to decompose at 160° C., is stable in the dark but releases oxygen in sunlight, and liberates iodine from potassium iodide solution.

Schiff (55) observed that turpentine which had been exposed to air appeared to contain an aldehyde. Blumann and Zeitschel (56) succeeded in isolating this substance and found that it was not an aldehyde but the dicyclic ketone verbenone. They also proved the presence of the corresponding secondary alcohol verbenol. Hence it appears that hydroxylation of the carbon atom alpha to the double bond occurs concurrently with the addition of oxygen.

Later work has shown that catalysts and temperature markedly influence

the relative rates of the two competing reactions. Weinhaus and Schumm (57) showed that osmium greatly increased the rate of formation of verbenol and verbenone, while Dupont and Zacharewicz (58) obtained mainly verbenone in the presence of cobalt abietate. Susuki (59) found that in the presence of oxides of lead, cobalt and manganese, pinene oxide was the principal product of the reaction below 20° C., while above 40° C. verbenol, verbenone and polymer were formed. A number of metals and their salts were found by Korotkov (60) to catalyze the absorption of oxygen by Russian turpentine, while other metals and their s alts inhibited the action. Substances which promoted the action were: iron, copper, zinc, Fe_2O_3, CuO, $CoCl_2$, and $MnCl_2$. Cook (61) found that the iron derivatives of some naphthocyanins promoted the formation of verbenol and verbenone.

Dupont and C rouzet (62) measured the rate of absorption of oxygen by pinene at constant pressure, and concluded that the reaction is autocatalytic. They found that sunlight increased the rate. Cobalt resinate was found to have a marked catalytic effect, while activated charcoal, ceric oxide, thoric oxide, and some of the common organic antoxidants exerted a retarding influence.

As pointed out on page 8, Schrauth (19) has patented a process for the oxidation of turpentine to maleic anhydride by passing its vapor mixed with air over a catalyst at elevated temperature. The patent specifies the use of from ten to fifty times the amount of air theoretically required. Dilution of the reaction mixture with nitrogen or steam also is mentioned, and operation at slightly above atmospheric pressure is stated to improve

the results. A temperature range of 250° to 500° C. is claimed to be allowable, and the patent states that ".... the range of temperature can be extended when a large excess of air is used. Hence rigid control is not necessary ...." Between 540° and 440° C. is mentioned as the most favorable range.

With regard to catalysts the patent allows considerable latitude. Best results are stated to be obtained with "..... oxides of polyvalent metals which form more or less stable compounds in several stages of oxidation and are of acid character, as for example vanadic acid and its salts, such as copper, silver, tin and bismuth vanadates ....." Oxides of molybdenum, tungsten, uranium, manganese and tin, as well as various combinations may be used. "..... As activating additions oxides of nickel, thorium, iron, copper, bismuth and cobalt have proved to be of considerable value ..... The effectiveness of the catalysts can be improved by the addition of inorganic oxygen acids, such as boric and phosphoric acids...."

The following example of the process is given: "Sulfate turpentine oil is sprayed into the reaction chamber at a temperature above 200° C. where it is mixed with hot air and passed in contact with a catalyst heated to 350° - 400° C. The catalyst may consist of vanadic acid on porcelain and may be activated with thorium oxide or phosphoric acid. The volume of air may approximate 100 cubic meters per kilogram of oil and its temperature as supplied should be such as to keep the temperature within the limits indicated.

If such a process could be developed to the point where economic yields could be obtained, it would provide an outlet for a considerable quantity of turpentine. With this in mind a research program was initiated which had

three principal objectives. These were : (1) to develop the apparatus and technique for carrying out the vapor phase catalytic oxidation of volatile organic liquids; (2) to obtain the fundamental data required to guide further research in this field; (3) to determine the optimum conditions for the oxidation of pinene to maleic anhydride and the maximum yield to be expected.

EXPERIMENTAL

I. NITROGEN OXIDES AS CATALYST

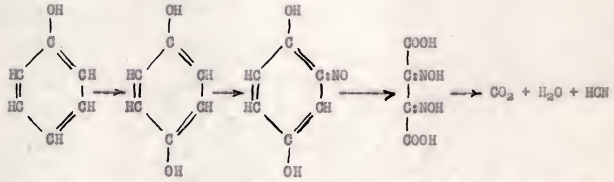
When this research was begun, the intention was to apply to pinene the method of Bibb and Lucas (7), whereby oxidation of hydrocarbons by air is catalyzed by nitrogen oxides acting as a homogeneous vapor phase catalyst. Accordingly, an apparatus was constructed similar to that employed by these workers. Its essential features were as follows.

Air from the laboratory mains was passed through a reducing valve and washing train into a reservoir, to which was connected a pressure regulating device. Three streams of air flowed from the reservoir through regulating stopcocks and flowmeters. One stream passed through a carburetor containing pinene, the second through a carburetor containing nitric acid, and the third passed directly to the reaction chamber. The carburetors were placed in separate thermostats held at constant temperature by mercury thermo-regulators. The three air streams combined at the entrance to the reaction chamber, which was of Pyrex glass, 2.5 centimeters in diameter and 15 centimeters long. The chamber was filled with broken porcelain, and was heated by an external winding of Nichrome wire. A thermocouple placed near the exit of the reactor served to indicate the temperature of the reacting gases. The treated gas mixture passed from the reactor through a condenser into a pair of water scrubbers.

The important variables and their means of regulation and measurement were: (a) rate of air flow, which was adjusted by means of stopcocks in the air lines and estimated from the readings of flowmeters in these lines; (b) ratio of pinene to nitric acid passed through the reactor, determined by the relative rates of flow of air through the two carburetors and by the temperatures of their respective thermostats; (c) ratio of air to pinene passed through the reac tor, determined by the relative rates of flow of secondary air (through the nitric acid, and directly to the reactor) and primary air (through the pinene carburetor), and by the temperature of the pinene carburetor; (d) the reaction temperature, regulated by adjustment of the current flowing through the heater winding on the reactor, and measured by means of the thermocouple.

A number of runs were made with this apparatus, using pinene as raw material, but the results were not promising and the method finally was abandonned in favor of that employing a solid catalyst. Control of the reaction temperature was found to be difficult, flame combustion and detonations occurring in many of the runs. Traces of aldehydes but no significant amount of acids were found in the reaction products. It was found that either substantially complete combustion occurred, or large amounts of tar were produced. It is interesting to note that traces of cyanides were detected in the product. This has been noted by other workers in the vapor phase nitration of phenols and quinones with nitrogen oxides, and was explained by Seyervets and Poizot (65). According to these workers, nitroso compounds are formed, and these are oxidized further with rupture of the

ring to form oximes of mesoxalic and dihydroxytartaric acids. The latter decompose into carbon dioxide, water and hydrogen cyanide. The same explanation could apply to the formation of cyanides in the oxidation of pineme in the presence of oxides of nitrogen, since aromatic compounds such as p-cymene can reasonably be expected to form to some extent under the experimental conditions, and subsequent oxidation of these through an hydroxylation mechanism would provide the phenols and quinones required in the following scheme.



It should be emphasized at this point that the inconclusive results obtained in this preliminary work with nitrogen oxides do not definitely rule out the possibility of achieving valuable results with the process. In fact, the greater familiarity with the oxidation reaction in general which was gained by the writer as a result of the work with solid catalysts has convinced him that further work with nitrogen oxides would be justified. In undertaking such work the important points to be borne in mind are these: (a) The concentration of NO_2 in the reacting gases should be kept low, preferably less than 2% of the total gas stream (64). Otherwise, the NO_2 acts not as a catalyst but as an oxidizing agent, becoming itself re-

duced and bringing about destructive oxidation of the reacting material. (b) A large excess of air should be used, such that the reacting gas stream contains about 100 mols of oxygen per mol of pinene. This is necessary in order to limit the reaction heat developed per unit of time per unit volume of reactor space. (c) The reactor preferably should be filled with a heat-conducting material such as granular aluminum, in order that the heat of reaction may be as evenly distributed and conducted to the walls as rapidly as possible. For this reason the reaction chamber should be of small diameter, 10 millimeters or less, and it should be immersed in a suitable bath held at constant temperature. By these means the reaction temperature could be adequately controlled. (d) Bearing in mind that at the temperatures necessary to initiate the oxidation reaction, a short time of contact of the reacting gases with the hot zone should be used. A time of contact of the order of half a second probably will be found necessary in order to obtain reasonable yields of partially oxidized products.

II .OXIDATION WITH A SOLID CATALYST

Choice of Catalyst

In commencing this study one of the first matters to be decided was the catalyst to be used. Vanadic acid is mentioned prominently in the Schrauth patent (18), but HVO_3 would be dehydrated to V_2O_5 under operating conditions, and the latter compound would be the actual catalyst. Furthermore, study of the literature of catalytic oxidation reveals that of the innumerable catalysts which have been tried only a very few have shown the ability to promote the formation of partial oxidation products. These are nearly all derived from elements of the fifth and sixth periodic groups, with vanadium pentoxide and salts of vanadic acid pre-eminent. In addition, most of the successful industrial applications of this process involve the use of vanadium pentoxide as catalyst. Accordingly, it was concluded that V_2O_5 would be the most promising catalyst for the oxidation of pinene, and it was therefore adopted. In addition, it was necessary to bring the scope of the investigation within bounds, and for this reason only one catalyst was studied. Details of its preparation are given in the section dealing with the preparation of materials.

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Development of Apparatus

The apparatus for carrying out vapor phase catalytic oxidation operates essentially as follows. Two constant measured streams of air, one carrying the vapor of the hydrocarbon being treated and designated as primary air, the other serving to bring the air-hydrocarbon ratio to the proper value and designated as secondary air, are mixed as they enter a reaction chamber containing the catalyst. This chamber must dissipate the heat of reaction, and at the same time it must be held within a narrow range of temperature. The treated gas stream leaving the reactor passes through condensers, scrubbers or other apparatus suitable for recovering the reaction product.

A considerable part of the effort expended on this study was devoted to the development of apparatus, and during the course of this development a number of difficulties were encountered. Therefore, it will doubtless be of value, especially to others who may carry on this work, to describe the various pieces of equipment tried and to point out the advantages and disadvantages of each.

1. Maintenance of constant Air Flow. -- In order to carry out the oxidation under controlled conditions, means must be provided for maintaining a constant rate of flow of air into the reaction chamber. Several methods for accomplishing this were tried before a satisfactory system was found.

The first arrangement tried depended upon the maintenance of constant pressure in the reservoir from which air was fed to the reaction chamber.

Assuming that resistances to flow in stopcocks, catalyst, scrubber, etc., remained constant throughout a run, maintenance of this pressure should ensure constant flow. The pressure regulator operated as follows: Air from the laboratory compressed air line passed through a reducing valve, thence through a capillary tube into a reservoir, and finally to the reactor. Connected to the reservoir was a regulating valve consisting of a jet opening beneath a column of mercury whose height could be adjusted by means of a leveling bulb. Accordingly, any increase of pressure beyond the value corresponding to the height of mercury above the jet would cause air to escape from the latter, thereby opposing the increase. While this system greatly reduced the fluctuations of flow due to variations of line pressure, it did not maintain a rate sufficiently constant for satisfactory operation.

The next arrangement tried depended upon the regulation of rate of flow rather than of pressure. To accomplish this a stopcock was placed in the air line leading to the reservoir. Across the stopcock was connected a manometer filled with a conducting aqueous solution and containing a wire so placed that contact was made with the solution when a given pressure differential existed between the two legs of the manometer. By adjusting the stopcock across the manometer the required pressure drop could be established when air was flowing at the desired rate. The electrical contacts in the manometer were connected to a thermionic relay which in turn actuated a magnetic valve connected to the air reservoir. When the rate of flow tended to exceed the value for which the apparatus was set, the circuit through the manometer was closed, causing the mag-

netic valve to open and allowing air to escape from the reservoir until the desired rate was restored. At this point contact in the manometer was broken, the valve closed, and the cycle was repeated.

This arrangement provided closer regulation than the mercury relief valve, but it had several disadvantages. It was found that using a fine opening in the air valve gave very constant flow when proper adjustments were made, but the apparatus would not handle the wide variations of line pressure which occasionally occurred. At peak pressures the rate of escape of air through the valve was not sufficient to restore the flow to its proper value. When a larger valve opening was used the rate of flow fluctuated up and down with the opening and closing of the valve. In addition it was found that adjustment of the stopcock across the manometer was very critical and required constant attention, thereby rendering the apparatus undependable. It was finally concluded that this arrangement probably would serve well only where a single constant rate of flow was desired. In this case the pressure drop across the manometer could be provided by a permanent orifice in place of the stopcock. Such an arrangement would not be suited for the present work, which required a flexible unit capable of being set at any desired rate.

The arrangement finally adopted is shown in the diagram of apparatus in Fig. 1. Air from the laboratory line passes through reducing valve V_1 and enters reservoir R_1 via capillary C_1. Connected to the reservoir is a mercury manometer M_1 provided with electrical contacts as shown. These contacts communicate w ith thermionic relay R, which is patterned after the manostat described by Herschberg and Hmtress (65) for maintaining constant reduced pressure in vacuum distillation equipment. The thermionic relay

operates magnetic valve V_2 which opens and allows air to escape from the feed line when the pressure in R_1 becomes sufficiently high to cause the circuit through manometer M_1 to be closed. As a result the pressure in R_1 oscillates over a range just sufficient to make and break the contact in M_1. Insertion of C_1, a six centimeter length of one millimeter capillary, was found to reduce these oscillations to the point where they were just discernable on mercury manometer M_2. The latter was inserted so that the pressure in the system could be observed. In normal operation flutter valve V_2 opens and closes sixty to eighty times per minute.

Following the units just described is a safety valve V_3 consisting of a tube communicating with the air line of the apparatus and opening under a column of mercury. In case the regulation system fails to operate, this valve allows air to escape from the system before the pressure can reach a dangerous value. The pressure at which air begins to escape is determined by the height of the leveling bulb B.

Before it enters the reaction chamber the air is freed of carbon dioxide by passing it through drierite and soda-lime in towers A_1 and A_2 respectively. It flows finally through reservoir R_3, which smooths out fluctuations to the point where they cannot be detected on the flowmeters.

2. Control of Air Flow .— Once constant pressure has been attained in the system the rates of flow of primary and secondary air are readily set and held at constant values by means of stopcocks S_1 and S_2. Capillaries C_2 and C_3 serve two purposes; they make the adjustment of S_1 and S_2 less critical by supplying part of the necessary pressure drop, and they prevent water from being blown out of the flowmeter manometers by limiting the air flow when S_1 and S_2 are wide open. With this arrangement the rate of

flow was found to remain constant over long periods of time, although in runs lasting several hours occasional adjustment of S_1 and S_2 was necessary.

In one run an obstruction in the scrubber caused by maleic acid crystals was suddenly released. This caused a surge of air which carried water from the flowmeter into the reactor, and shattered it. Following this, trap T_1 was inserted in the line to prevent such an eventuality.

3. Measurement of Air Flow.— The rates at which primary and secondary air enter the reactor are measured by flowmeters F_1 and F_2 respectively. Such a meter consists of a short capillary in the air stream which introduces a pressure drop proportional to the rate of flow. The pressure drop is indicated by a water manometer connected across the capillary. In the construction of these meters capillaries were prepared by drawing out lengths of glass tubing and testing them until sizes were found which gave the proper manometer readings at the desired maximum rates of flow.

Suitable capillaries having been selected, it was necessary to calibrate them. This was done as follows The downstream or outlet side of the meter was connected by means of rubber tubing to the top of a ten liter aspirator bottle. The asptrator bottle was elevated above the work bench to provide head sufficient to obtain the desired flow, and in order that the fractional change in head due to the fall of the water level during a determination should be as small as possible. The head was further increased by connecting a rubber tube to the outlet of the aspirator and al-

lowing it to reach a container on the floor. At the end of this tube were placed a pinch clamp for quickly starting and stopping the flow of water, and a screw clamp for regulating the rate of flow.

Measurements were made by filling the aspirator with water and then allowing it to empty at a uniform rate, air entering through the flowmeter to replace the water. Simultaneous readings were made of the flowmeter manometer and the time required for a given volume of water to flow from the system. From twelve to twenty-four measurements were made at each rate. Two meters were calibrated in this manner, while a third was calibrated by connecting all three in series and recording simultaneous manometer readings at various rates. The third meter was made originally for use in the experiments on nitrogen oxides, in which three streams were necessary. It was used also in the runs with vanadium pentoxide when high rates of flow were desired. This was accomplished by connecting two meters in parallel.

After making the measurements just described, a curve was constructed by plotting the logarithm of rate of flow[1] (liters per minute) against the meter reading in arbitrary units. (One unit = approximately 5 mm. of water). A straight line was drawn through the points for which an equation was derived. Even values of meter reading were substituted in the equation and corresponding values of rate of flow were calculated. These are listed in Table III and are plotted in Figs. 2 and 3.

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[1]Actually the logarithm of ten times the rate of flow was plotted, in order to avoid negative logarithms. This explains why the factor 10 appears in the equations.

Meter No. 1 and meter No. 2 were found to have critical rates of flow, above which the air could be heard flowing through the orifice and below which it was inaudible. At these rates the manometer readings were unstable. Because of the way in which the capillaries were made no estimate could be made of their diameter, and hence Reynolds numbers could not be calculated. However, it is probable that these critical points lie in the range where the flow changes from streamline to turbulent. For this reason the meters were used below the critical rates wherever possible. The accuracy in this range is probably about 2%. It probably is somewhat less above the critical rate.

Table II. Flowmeter Calibrations.

Meter Reading, Arbitrary Units. I Unit = Approx. 10 mm.	Rate of Flow in Liters Per Minute		
	Meter No. 1	Meter No. 2	Meter No. 3
0	0.000	0.000	0.000
1	0.148	0.205	0.207
2	0.257	0.310	0.315
4	0.379	0.475	0.479
6	0.501	0.610	0.612
8	0.608	0.728	0.730
10	0.708	0.834	0.836
15	0.933	1.069	1.069
20	1.135	1.276	1.274
25	1.321	1.462	1.459
30	1.496	1.637	1.630

These data are represented by the following equations.

		Critical Points	
		Meter Reading	Rate of Flow
Meter No. 1.	$\log (10\ R) = 0.681 \log H + 0.169$	25.0	1.321
Meter No. 2.	$\log (10\ R) = 0.614 \log H + 0.507$	18.5	1.216
Meter No. 3.	$\log (10\ R) = 0.607 \log H + 0.515$	None observed	

H = meter reading. R = rate of flow in liters per minute.

4. Measurement of Reaction Temperature. — In a heterogeneously catalyzed reaction in which a large amount of heat is developed, the measurement of the actual temperature at which reaction occurs presents a difficult if not insurmountable problem. This is due to the fact that the reaction occurs in limited areas of catalyst surface, with the result that large temperature gradients must exist in order that the heat developed in these restricted areas may be transferred through the catalyst mass to the walls of the confining tube. As an example, Reid (86) reports that in experiments with "hopcalite", a catalyst used in gas masks to convert carbon monoxide to carbon dioxide, microscopic examination of samples of catalyst which had been exposed to mixtures of carbon monoxide and air at room temperature revealed that portions of the surface actually had fused. This indicated that temperatures hundreds of degrees above the measured temperature must have existed when reaction was occurring. A similar observation was made in the course of the present investigation. Several runs were made in which vanadium pentoxide catalyst was fused, despite the fact that the measured temperature of the reacting gases was at least 350° C. below the fusion temperature of V_2O_5.

In view of these difficulties, no attempt was made in this study to measure the actual surface temperature of the catalyst. In the early experiments, in which a directly heated reaction tube was used, the temperature of the gas mixture was measured at the point where it emerged from the catalyst mass. In the later experiments, which constitute the major portion of the work, the temperature of the bath surrounding the reactor was measured. This was done

in full cognizance of the limitations involved.

Because the temperature to be measured was above the range of the ordinary mercury-in-glass thermometer, use of thermocouples was resorted to. These were made from No. 28 B. & S. gage copper and constantan wires, fused together in the blast lamp, using borax as flux. The thermocouple consisted of two junctions, one maintained at 0° C. and the other raised to the temperature to be measured. Both junctions were protected by inserting them into thin walled glass tubes. Electrical insulation of the lead wires was provided by lengths of finely drawn glass tubing drawn over them. The hot junction was protected against oxidation by packing the tube containing it with powdered alumina, as suggested by Wood and Cork (67).

The electromotive force developed by the thermocouples was measured by means of a Hoskins pyrometer. However, the pyrometer available was not scaled in terms of copper-constantan, and calibration was necessary. This was done by comparing the pyrometer reading with the reading of a standard thermometer when the hot junction and the thermometer were immersed in a well stirred bath and the cold junction was immersed in ice and water contained in a Dewar flask. Readings were taken while the bath was heating and while it was cooling, in order that any tendency to lag would be noted. To obtain points above 360° C., the maximum temperature possible with the standard thermometers, the meter reading was noted when the hot junction was at the melting point of potassium dichromate (398° C.), the freezing point of zinc (419° C.), and the freezing point of antimony (630° C.) (67). The

thermometers used had been checked by the Bureau of Standards. Two pyrometers were calibrated. These were No. P6A1 and No. P6A2 (Department of Chemistry stock numbers). Temperatures corresponding to rounded values of pyrometer reading are listed in Tables III and IV. Calibration curves are shown in Fig. 4.

Table III. Pyrometer Calibration. Pyrometer No. P6A1.

Copper-Constantan Thermocouple

Pyrometer Reading	Temperature °C.
75	137
100	217
125	287
150	317
175	367
200	417
225	467
250	517

Table IV. Pyrometer Calibration. Pyrometer No. P6A2.

Copper-Constantan Thermocouple

Pyrometer Reading	Temperature °C.
100	110
200	189
300	268
400	347
500	426
600	505
700	584

5. Hydrocarbon Feed.— In devising a means for feeding hydrocarbon into the reactor, three possibilities suggest themselves. (a) The liquid hydrocarbon may be allowed to drip at a uniform measured rate into the reactor, where it will vaporize into the air stream. (b) The hydrocarbon may be boiled at a fixed rate and the vapor passed into the reactor. (c) Part of the incoming air stream may be passed through a carburetor containing the hydrocarbon at a definite temperature. The latter method is most feasible when extremely small rates, of the order of one to two grams per hour are required. It was therefore adopted, and has proven to be very satisfactory.

The carburetor consists of three parts, as indicated in Fig. 1. The air enters through a coil of six millimeter tubing which serves to bring the temperature of the air to that of the thermostat in which the carburetor is immersed. After leaving the coil the air passes through two bubblers 2.5 centimeters in diameter and 10 centimeters long, containing the hydrocarbon, and in which saturation of the air occurs. For the sake of clarity these three parts of the carburetor are shown in line in the diagram. Actually, however, they are arranged in a triangle so that the assembly can be handled as a single compact unit. Connection with the flowmeter is made by means of rubber tubing, while the outlet of the carburetor is joined to the reactor by means of a standard taper glass joint. With this arrangement the carburetor is readily removed for filling and weighing. By weighing it before and after a run, the amount of hydrocarbon fed is accurately measured.

The equipment for maintaining the temperature of the thermostat is not shown in the diagram. This consists of a stirrer, a knife heater, a

mercury thermo-regulator and relay for controlling the heater, and a copper coil through which cold water may be circulated when the thermostat is to be operated below room temperature. On warm Summer days it is necessary to run the cooling water through an ice bath if it is desired to operate below 30°C.

That equilibrium was established when pinene was used in the carburetor was shown by the agreement between the amount of pinene actually evaporated and the amount calculated from the rate of flow and the vapor pressure of pinene at the temperature of the carburetor thermostat. In making such calculations and in estimating the setting of the apparatus to give a predetermined rate of feed, the vapor pressure data of Pickett and Peterson were used (68).

6. The Reaction Chamber.— The reaction chamber to be used in an oxidation reaction must be designed with great care. This is evident when one considers that the reaction involved is highly exothermic, especially in processes like the conversion of pinene to maleic anhydride where considerable portions of the molecule are oxidized off. In addition the temperature of the catalyst must be held within narrow limits if maximum yields are to be obtained. In the commercial production of phthalic anhydride, for example, the heat theoretically evolved in the reaction is 5460 B.T.U. per pound of product. In actual practice some complete combustion occurs, so that according to Weiss and Downs (69) the heat evolved actually is about 10,000 B.T.U. per pound of product (5,560 calories per gram of product). Unless this heat is dissipated the catalyst temperature rises to the point where complete combustion occurs. The effect is cumulative, in that the poorer the tempera-

ture regulation the more hydrocarbon is burned, and the greater is the tendency for the temperature to rise. As a consequence, progress in the technology of hydrocarbon oxidation has been measured largely by improvements in the design of converters. In fact the large scale application of the process dates from the introduction of the Downs converter (70), which employs a boiling liquid such as mercury or diphenyl as a heat absorbing and temperature regulating medium.

In the first experiments on pinene oxidation with vanadium pentoxide catalyst, it was thought that in small laboratory apparatus radiation of heat could be depended upon to maintain the desired temperature in the reactor. In fact, in small tubes the ratio of surface area to volume is large, and therefore thermal insulation and heat input are necessary.

Accordingly, a reactor was made of Pyrex tubing 2.5 centimeters in diameter and 20 centimeters long, with a 15 centimeter packed section. Two inlet tubes 5 millimeters in diameter were sealed tangentally to one end of the reactor. In this way the entering streams of air were given a spiral motion which ensured thorough mixing. At the exit end a ground joint was provided for connecting to the product recovery apparatus, and a thermocouple well projected into the re ctor in such a way that the temperature measured was that of the reacting gases immediately after they emerged from the catalyst zone. The reactor was wound with Nichrome wire and covered with asbestos insulation. A rheostat in series with the heater winding provided temperature control.

A number of runs were made with this reactor, but the results were not satisfactory. At the start of an experiment current was passed through the heater until the desired temperature was reached. Then the pinene-air mixture

was started through the tube. As soon as the reaction commenced the temperature rose rapidly, and it was not possible to balance the heat input against the radiation loss with sufficient accuracy to maintain a stable reaction temperature. Considerable experimentation with this arrangement made it evident that thermostatic control was necessary. The simplest way to accomplish this is to immerse the reactor in a bath held at the desired temperature, and accordingly this was done.

The first reactor prepared for this purpose consisted of three Pyrex U-tubes connected in parallel by means of manifolds. Ground glass joints for connecting accessory apparatus were sealed to the manifolds. The U-tubes were 1.35 c entimeters inside diameter, with legs 18 centimeters in length. The entrance legs of the U-tubes were packed for a distance of 17.5 centimeters with aluminum pellets, while the exit legs contained the catalyst over a 12.5 centimeter length. The total volume of the catalyst space was 61 cubic centimeters, and the free volume was 36.6 cubic centimeters. Several runs were made with this reactor and the trend of yields indicated that the shortest contact time obtainable with the flowmeters at maximum rate was above the range for optimum yield. Consequently a reactor with a smaller catalyst volume was required.

The reactor finally adopted is shown in Fig.1. It consists of a single U-tube 15 millimeters in diameter, with legs 15 centimeters long. The entrance leg is packed for a distance of 12.5 centimeters with random size aluminum balls (approximately 5 millimeters in diameter) to preheat the incoming gas, while the exit leg is packed with catalyst over an equal distance. The total catalyst volume is 16.6 cubic centimeters and the free volume is

60% of the total, or 9.96 cubic centimeters. Standard taper glass connections are provided for joining the reactor to the secondary air inlet, the carburetor and the product recovery system. The connection to the carburetor is wound with a few turns of Nichrome wire, in order that it may be heated to prevent the condensation of hydrocarbon when the pinene carburetor is operated above room temperature.

7. The Reactor Bath.— The high temperature at which the reactor was to operate imposed severe limitations upon the types of materials which could be employed as bath fluids. Fused metals and fused salts offered about the only possibilities. The ternary eutectic of sodium nitrate, potassium nitrate and calcium nitrate has the advantages of relatively low freezing point, density and viscosity, together with high heat conductivity and low cost. Hence it was adopted, and has served the purpose adequately.

Menzies and Dutt (71) have constructed the freezing point diagram for this system. Their data for the ternary eutectic are given in Table V. The relative weights of the three salts to be used were calculated from these data and are included in the table. Listed also are the melting points and decomposition temperatures of the pure salts (72). The temperatures at which the bath was used were above these decomposition points but this caused no trouble. That some decomposition did occur was shown by the fact that samples of the bath after several months' use showed an alkaline reaction when dissolved in water. In addition, glass apparatus exposed to the bath was slightly etched.

Table V. Ternary Eutectic of $NaNO_3$, KNO_3, $Ca(NO_3)_2$

Compound	Melting Point °C.	Decomposition Temperature	Mol % In Eutectic	Molecular Weight	Weight Taken Grams.
$NaNO_3$	308	380	20	85	1700
KNO_3	333	400	45	101	4540
$1/2\ Ca(NO_3)_2$	561	---	35	82	2870

The first bath container which was used consisted of a one liter beaker wound with Nichrome wire and thoroughly insulated with asbestos. It was discovered, however, that although the salt mixture shrinks in volume when it freezes it adhered to the glass container with sufficient tenacity to break it. Therefore a container was made from sheet iron, with all joints carefully brazed. It was wound with asbestos paper for electrical insulation, and this was covered with a winding of Nichrome wire designed to provide 600 watts at 110 volts. The whole was enclosed in a can packed with asbestos powder to provide thermal insulation.

This bath failed after a few runs, and when it was dismantled it was found that the asbestos insulation had failed, allowing an arc to develop which cut through the can. A second, more thoroughly insulated bath was made, and failed in the same manner after a short period of use. The trouble finally was traced to salt creeping over the top of the bath and working into the asbestos insulation rendering it electrically conducting. A metal flange at the top of the bath prevented this and a bath so protected was used constantly for several months without giving any trouble. The bath shown in

Fig. 1 is 10 centimeters in diameter and 20 centimeters high.

Several attempts were made to devise thermo-regulators for the salt bath. The first system tried consisted of a thermocouple immersed in the bath and connected to a meter on the scale of which was mounted a movable contact. The contact, set at the proper place on the scale, was to close a circuit through the meter needle when the temperature reached the appropriate value. The contact was connected to a thermionic relay which operated a switch in the heater circuit. However, the contact required was found to be too delicate and hence not dependable.

The next method attempted depended upon control of the heater circuit by a contact in a mercury manometer connected to an air bulb in the bath. This system was more positive in action than the previous one, but it was found to permit a gradual drift of temperature.

Another difficulty in such systems is the lag in the heater. The lag is caused by the thick layer of asbestos paper which is necessary to prevent short-circuiting of the heater winding through the metal container. Response of the bath temperature to the thermo-regulator therefore is extremely slow, with the result that close regulation is impossible. Accordingly it was finally concluded that manual regulation of the bath temperature would be most satisfactory. After some practice in order to gain familiarity with the response of the bath temperature to changes in the rheostat setting, it was possible to hold the temperature constant to within plus or minus 5° C.

8. Product Recovery. -- The recovery of organic compounds from the gases issuing from the reaction chamber presented no serious difficulties.

Maleic anhydride, the product sought, is partly converted to maleic acid by combination with water vapor when the treated gases are cooled, and scrubbing with water completes the conversion. The maleic acid so formed is extremely soluble in water. Hence it is effectively removed by water scrubbing. The solubility of maleic acid in water is given in Table VI (73).

Table VI. Solubility of Maleic Acid In Water.

Temperature	Solubility g. Acid / 100 g. H_2O
25	78.8
40	112.5
60	148.7
97.5	392.6

Formaldehyde, the other principal product detected, also is extremely soluble in water. Since it is a gas at the temperature of the scrubber, the amount which escapes with the excess air will depend upon the partial pressure of formaldehyde over the aqueous solution in the scrubber. With the scrubber at 0° C., and at the low concentrations obtained in the course of a run, the partial pressure and consequently the loss of formaldehyde is negligible, as shown by the data in Table VII (74).

Table VII. Partial Pressure of Formaldehyde Over Aqueous Solutions at 0° C.

Weight % Formaldehyde	Partial Pressure, mm.
5	0.057
10	0.070
15	0.098
20	0.120

Design of scrubbers involved some difficulty. The first units used were made tall and narrow with the object of providing the maximum contact between the gas stream and the scrubber liquid. These scrubbers were 2.5 centimeters in diameter and 20 centimeters tall. Troublesome frothing occurred in some runs in which they were used, and this carried scrubber solution out with the exit gas. This was overcome by making the diameter of the scrubbers larger, but since it was desirable to limit the total amount of scrubber solution to 200 ml or less in order to allow for washing and making up to 250 ml for analysis, the height of the scrubbers was at the same time reduced. Those shown in Fig. 1 are 4.5 centimeters in diameter and 15 centimeters tall.

The cold trap shown in the figure requires no comment. It is approximately 1.5 centimeters in diameter and 18 centimeters tall. Its dimensions are governed by those of the Dewar flask in which it is immersed.

In some runs, particularly those at high rates of flow and in the low temperature range, a dense fog was produced which was difficult to collect. It passed unhindered through all scrubbers and traps which were tried, the reason being that the fog was composed of water insoluble liquid products condensed in extremely fine particles. An electrical precipitator, consisting of two vertical concentric aluminum cylinders connected to the terminals of a spark coil, with the exit gas passed through the annular space between them, precipitated only a portion of the fog. Such a precipitator should of course be excited by high voltage direct current, and in the absence of the necessary equipment it was abandoned in favor of other methods.

The most effective means for the precipitation of the fog consisted of passing the exit gases through a trap filled with activated charcoal, and by this means it was determined that the weight of material contained in the fog was small. When a 1.5 meter length of 7 centimeter tubing was connected to the outlet of the apparatus, the velocity of the exit gas was reduced to the point where a considerable portion of the fog collected on the walls as a viscous yellow liquid. In this way a composite sample representing several runs was obtained in sufficient quantity to permit some chemical examination.

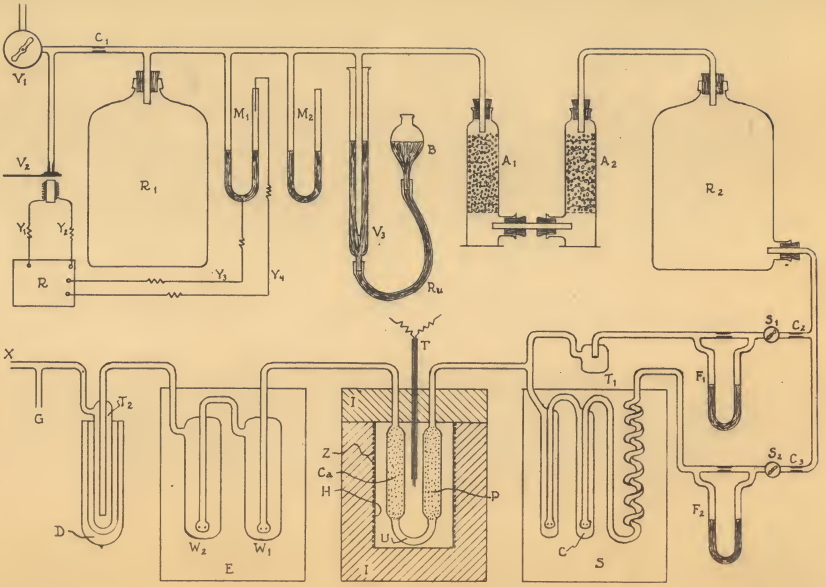
C1
V1
V2
R1
M1
M2
B
A1
A2
R2
Y1
Y2
R
Y3
Y4
V3
Ru
T
X
G
T2
D
W2
W1
E
J
Z
Ca
H
P
U
I
T1
F1
S1
C2
C3
F2
C
S

Fig. 1.

Operation of Apparatus.

The reactor bath requires about three hours to heat from room temperature to 400° C., and therefore it is necessary to begin heating several hours before a run is to start. During one period of intensive work on this project when one or two runs a day were being made, the heater was left on the line all night with a current of 1.5 to 2 amperes flowing. The following morning it was possible to bring the bath to reaction temperature within an hour.

While the bath is heating the apparatus can be prepared for assembly. Hydrocarbon is poured into the carburetor until the bubblers are about half full, thereby allowing sufficient space above the liquid to prevent its being carried over mechanically by the air stream. The glass stoppers are placed firmly after being coated with an oil insoluble stopcock grease+. The carburetor is then weighed to within 50 mg. If properly filled it s hould weigh about 185 grams.

In filling the water scrubbers, 70 ml. of distilled water are placed in the first scrubber and 90 ml. in the second, since some water is formed in the reaction and condenses in the first scrubber.

+The oil insoluble grease was prepared according to directions in the Chemical Formulary, Vol. III, p. 215. It consists of glycerine, dextrin and mannitol.

As soon as the salt bath has melted, the reactor is put is place. It should be pointed out that the salt mixture is very hydroscopic, and if a coating has been left on the reactor for any length of time it will have become covered with moisture. If the tube is immersed in the bath in this condition it may be cracked. Therefore all glass parts should be rinsed off with water and thoroughly dried before they are placed in the hot bath. The risk is further reduced by placing such parts in the bath as soon as it has melted, since its temperature then is around 175-180° C.

As soon as the reactor is in place, the remainder of the apparatus can be set up. The secondary air connection is secured to the reactor, and the carburetor is immersed in the thermostat and connected to the reactor by means of its ground joints. Connection between the flowmeter and the reactor is made with rubber tubing, rubber-glass connections being sealed with glycerine. The scrubbers are connected to the reactor through the ground joint provided for that purpose, and the insulating lid, thermocouple and stirrer are set in place on the salt bath. The cold trap is immersed in a Dewar flask containing a freezing mixture of ice and concentrated hydrochloric acid, and is joined to the scrubbers by means of rubber tubing. The thermocouple cold junction is immersed in a mixture of ice and distilled water in a Dewar flask, and cracked ice is packed around the scrubbers. The apparatus then is ready for operation, provided the thermostat and salt bath have reached the desired temperatures.

Some care must be exercised in starting the run. If the secondary air stream is started first the back pressure due to the scrubbers may back up the hydrocarbon in the carburetor. Hence it is well to start the primary air stream slightly ahead of the secondary stream. The time at which flow is started is recorded, and the rates of flow are immediately set at the proper values. Before setting the flowmeters the inner walls of the manometers should be wet, since it has been observed that if the tube is dry immediately above the meniscus an entirely erroneous reading may be made. The tube may be wet by causing the water to surge up and down a few times by suitable manipulation of stopcocks S_1 and S_2.

Within a few minutes after the reaction starts the reactor bath temperature will begin slowly to rise, unless proper adjustment has been made of the rheostat in the heater circuit. A little practice is necessary before these adjustments can be made in such a way as to hold the temperature at the proper value, since detectable changes in temperature may lag behind rheostat adjustments by as much as 10 - 15 minutes.

At intervals during the course of the run the following entries are made in the notebook: (1) time, (2) the two meniscus levels in the primary air meter, (3) the same data for the secondary air meter, (4) the pyrometer reading, (5) the air temperature indicated by a thermometer hung on the flowmeters, and (6) remarks.

At the conclusion of the run the primary air is cut off, and the time noted. The secondary air stream is allowed to continue flowing for about 5 minutes to sweep out the catalyst tube. The apparatus must then be completely dismantled, since any glass parts left in the salt bath will be shattered when the latter freezes.

Preperation of Materials.

1. Pinene.— Pure pinene is best prepared by fractionating wood turpentine. This is a more suitable starting material than gum turpentine becauseit contains no nopinene, a compound which comprises about 20% of gum spirits. Pinene boils at 156° C. and nopinene at 165° C., hence separation of the two isomers requires a column containing many equivalent plates. On the other hand, the principal constituents of wood turpentine other than pinene are monocyclic terpenes boiling at 170 - 175° C., and polymer which boils at much higher temperatures. Separation of pinene from this mixture therefore can be accomplished with a fractionating column equivalent to about 10 or 12 plates.

Hercules commercial alpha pinene, which is derived from wood turpentine,was used as starting material. It was given a simple distillation to remove water, and oxygenated compounds which decompose to yield water when heated. This eliminated the troublesome deposition of water in the head of the column when the material was fractionated, a circumstance which interferes with smooth fractionation and proper determination of boiling points. This preliminary distillation also served to remove most of the high boiling material. The first runnings of the distillation were returned to a subsequent batch, and the remaining clear distillate fractionated. The pinene obtained by this method had the following constants:

Boiling point at 760 mm.	155 - 156° C.
Density at 30° C.	0.856
Refractive index at 30° C.	1.4658

2. Dipentene.— Hercules commercial dipentene was distilled as was the pinene, and the clear distillate fractionated. The dipentene fraction had the following constants:

Boiling point at 760 mm.	175 - 176° C.
Density at 30° C.	0.840
Refractive index at 30° C.	1.4720

3. p-Cymene.— Eastman "p-cymene, technical" (spruce turpentine), a very crude product containing dissolved sulfur dioxide and much high boiling material, was the source of the p-cymene used. It was distilled to remove most of the high boiling constituents, and the distillate was extracted with small portions of 95% sulfuric acid to remove unsaturated compounds. This is necessary because the monocyclic terpenes which are present have boiling points almost identical with that of cymene, and hence cannot be separated by fractionation (75). The extract was washed with 10% caustic soda solution, distilled and fractionated. The cymene cut had the following constants:

Boiling point at 760 mm.	174 - 175° C.
Density at 30° C.	0.850
Refractive index at 30° C.	1.4900

An attempt was made to prepare p-cymene by dehydrogenation of dipentene with selenium. One mol of dipentene and one mol of selenium were refluxed in an apparatus containing caustic soda traps to prevent escape of H_2Se into

the laboratory. After refluxing for about 24 hours the selenium had only partly reacted, and the product still contained much material soluble in c oncentrated H_2SO_4. The method was not investigated further, but it appears that p-cymene could be prepared in this manner by conducting the reaction in an autoclave, and therefore at a higher temperature.

4. Standard Alkali.— A saturated NaOH solution was prepared by dissolving c.p. NaOH in hot water and holding the solution near 100° C. for several hours in a closed container immersed in boiling water. At this temperature the viscosity of the solution was low enough to allow the precipitated sodium carbonate to settle. The solution was allowed to cool, and the supernatent clear liquid was decanted from the layer of carbonate and NaOH crystals on the bottom. The carbonate-free concentrated solution thus obtained was stored in paraffin coated bottles. Standard N/10 alkali solution was prepared by diluting this solution with the requisite amount of water. The N/10 solution was standardized by titration against Bureau of S tandards potassium hydrogen phthalate.

5. Standard Acid.— Tenth normal hydrochloric acid was prepared by diluting the c.p. concentrated acid. It was standardized by titration against the alkali.

6. Vanadium Oxide Catalyst.— In the preliminary runs in which a directly heated reactor was used, the catalyst was solid V_2O_5, without support. It was prepared by heating ammonium metavanadate in a crucible over a direct flame until it was completely decomposed and the resulting oxide had fused.

This was allowed to solidify, and the mass was broken up with a hammer and screened to provide 3 - 4 mm. grains. The sized material was packed directly into the reaction chamber.

In all the runs for which data are reported, the catalyst was prepared essentially as directed by Milas and Walsh (76), using granular pumice as support. The pumice was screened so as to obtain 5 mm. particles, since sizes larger than this were found to pack unevenly in the small catalyst tube, leaving large voids near the walls. In a typical preparation, a solution was prepared by dissolving 20 grams of technical ammonium metavanadate in a hot mixture of one liter of water and 500 ml. of c.p. concentrated ammonium hydroxide. This solution was added gradually to 45.5 grams of the pumice support in an evaporating dish on the steam bath, until all of the water had evaporated and the pumice was impregnated with ammonium metavanadate. The impregnated pumice was heated over a burner in an air bath made of two concentric crucibles, until decomposition of the ammonium salt was complete. The pumice was thus coated with vanadium pentoxide:

$$2\ NH_4VO_3 = V_2O_5 + H_2O + 2\ NH_3$$

At this stage the catalyst had a bright orange-red color.

According to Milas and Walsh (76) the freshly prepared catalyst is too active, and tends to promote the complete oxidation of hydrocarbons. For this reason it was packed into the reactor and a pinene-air mixture passed through it for several hours at a temperature of 350 - 400° C. In the course of this treatment the color of the catalyst changed to a bluish-black, indicating that changes in structure or composition had occurred. Following

this "seasoning" the catalyst was considered ready for use.

The "free volume" of the catalyst was determined by packing a sample into a tube of the same diameter as the reactor and measuring the volume of xylene necessary to fill the voids. This yielded the following data:

Total or "apparent volume" of catalyst:	100 ml.
Xylene required to fill voids	60 ml.

The free volume of the catalyst therefore is 60% of the apparent volume.

Analysis of Product.

After completion of a run, the solutions from both scrubbers and the condensate in the cold trap were transferred quantitatively to a 250 ml. volumetric flask. The dark colored resinous deposit which formed in the reactor exit was washed into the flask with a little alcohol. The crystals of maleic ac id which deposited on the inner walls of the tube leading into the first scrubber likewise were washed into the flask. Scrubbers, cold trap and reactor tube exit were rinsed with distilled water and the rinsings added to the flask. The solution thus obtained was made up to volume and aliquots withdrawn for analysis. In case water-insoluble oils were formed, these collected on the surface and were removed with a micro pipette before making up the solution to volume.

In order that aliquots could be withdrawn accurately from the volumetric flask, a 10 ml. pipette, a 25 ml. pipette, and the flask were calibrated in the usual way with distilled water. The data are given in Table VIII.

Table VIII. Calibration of Volumetric Glassware.

Temperature 21.5° C.

Item	Contains ml.	Delivers ml.	Ratio	
			Flask:Pipette	Pipette:Flask
250 ml. Flask	249.21	------	------	------
10 ml. Pipette	------	10.00	24.92	0.04012
25 ml. Pipette	------	25.00	9.97	0.1003

1. Maleic Acid.-- A sample of pure maleic acid for purposes of comparison w as prepared by dissolving commercial maleic anhydride in hot water, allowing it to cool, and collecting the maleic acid which crystallised out. The acid was recrystallised from water and dried at 110° C. The melting point was 134 - 135° C. (sealed tube).

A reference sample of fumaric acid was prepared by adding a drop of bromine to the mother liquor from the maleic acid preparation and exposing the solution to bright sunlight for an hour. The fumaric acid which precipitated was recrystallized from water and dried at 110° C. It melted at 295 - 297° C.

Maleic acid was identified qualitatively by means of the following proceedure. The scrubber solution was evaporated to a small volume, in the course of which the liquid became very dark in color. It was treated with decolorizing carbon and filtered through a close-grained paper. The filtrate was extracted seven or eight times with small portions of ether, and the maleic acid recovered by evaporation of the ether. The acid thus obtained was dissolved in hot alcohol and benzene was added to incipient precipitation. The solution was allowed to cool and crystallize. The crystals were filtered off and dried at 110° C. The melting point of the acid thus obtained was 134 - 135° C.

The distribution of maleic acid between water and ether does not favor extraction. Hence the above proceedure removed only a portion of the acid from the aqueous solution. The maleic acid remaining in solution was isomerized to fumaric acid by adding bromine and exposing the solution to bright sunlight. The crude fruaric acid was filtered off,

recrystallized from water, and dried at 110° C. Its melting point was 295 - 297° C.

Another method employed for removing maleic acid from the product involved the precipitation of barium maleate monohydrate by a procedure similar to that outlined for the quantitative estimation of maleic acid. The barium salt was dissolved in dilute HC l and the Barium was precipitated with sulfuric acid. After filtering off the barium sulfate the solution was extracted with ether as before.

After qualitative tests showed that maleic acid was the principal product of the oxidation of pinene, it was necessary to devise a method for its quantitative estimation. The first method considered was that of Milas and Walsh (76), which depends upon the insolubility of barium maleate monohydrate in an alcohol-water mixture. The procedure was first applied to a known sample of approximately the same concentration as that obtained in the oxidation. This solution was prepared by dissolving 4.000 grams of the purified maleic acid in water and making up to volume in the calibrated 250 ml. volumetric flask. Ten ml. of this solution was withdrawn with the calibrated pipette and measured into a 100 ml. beaker. The sample was made just alkaline to litmus with ammonia and 4 ml. of barium chloride was added (1 ml. = 0.1 g. $BaCl_2.2H_2O$). Fifty ml. of 95% alcohol was then added while stirring, whereupon the barium salt precipitated. The precipitate was filtered in a Gooch crucible, dried at 110° C. and weighed.

Following this the barium content of the salt was determined by dissolving the precipitate in dilute HCl and precipitating the barium as barium sulfate.

Calculations were made as follows.

Molecular Weights:

Maleic Acid $H_2C_4H_2O_4$	116.04
Barium Maleate Monohydrate $Ba.C_4H_2O_4.H_2O$	269.40
Barium Sulfate $BaSO_4$	233.42
Barium Carbonate $BaCO_3$	197.46
Barium Ba	137.36

Gravimetric Factors:

Barium Maleate Monohydrate to Maleic Acid	0.4307
Barium Sulfate to Barium	0.5885
Barium Carbonate to Barium	0.6960

The weight of maleic acid corresponding to the precipitate of barium maleate monohydrate is given by the expression:

$$\text{Maleic Acid} = \frac{\text{wt. of ppt.} \times 116.04}{269.4},$$

and since the ratio of the volume of the flask to that of the pipette is 24.92, the factor for converting the weight of barium salt to the total weight of maleic acid in 250 ml. is-

$$\text{Factor} = \frac{116.04 \times 24.92}{269.4} = 10.73$$

The gravimetric factor for converting the weight of barium sulfate to the equivalent weight of barium is 0.5885. Therefore the barium content of the salt is given by the expression:

$$\text{Ba Content} = \frac{\text{Wt. of } BaSO_4 \times 0.5885 \times 100}{\text{Wt. of Ba maleate}}.$$

The results of analyses on the known solutions are given in Table IX.

Table IX. Analysis of Known Maleic Acid Solutions.

4.000 g. of Maleic Acid in 250 ml. of Solution.

Ratio of Total to Aliquot Analyzed = 24.92.

	Sample 1.	Sample 2.	Sample 3.	Mean
Wt. of $BaC_4H_2O_4.H_2O$	0.5472 g.	0.5744 g.	0.5742 g.	0.5743 g.
Total Acid Calcd.	4.015 g.	4.017 g.	4.015 g.	4.016 g.
Wt. of $BaSO_4$	0.5195 g.	0.5195 g.	0.5220 g.	0.5203 g.
% Ba Calculated	50.22 %	50.22 %	50.64 %	50.36 %

Calculated for $Ba.C_4H_2O_4.H_2O$ Ba = 50.9%

Any method of analysis involving a gravimetric procedure is slow and tedious. Therefore, in view of the large number of runs required to establish the optimum conditions for the production of maleic acid, a more rapid method of analysis was found. Several runs were analyzed by the gravimetric procedure and the yields so obtained were compared with those determined by titrating an aliquot with standard alkali, using phenolphthalein as indicator. The agreement between these methods showed that acids other than maleic were not formed in significant amounts, and that titration could be relied upon as a measure of maleic acid yield. Accordingly, titration was used to determine the yields in all runs. The final runs at optimum yields, as well as those with dipentene and p-cymene, were checked by the gravimetric procedure, however, and the two methods were in reasonable agreement. The barium content of the precipitate was determined as before, and this supplied further evidence for the identity of the acid.

In titrating the scrubber solutions a 10 ml. aliquot was used, and

phenolphthalein was employed as indicator. It was noted that color bodies were present in the solution which darkened as alkali was added, thereby tending to obscure the end point. It was found that this difficulty could be at least partially overcome by diluting the sample with about 100 ml. of water before titrating.

The alkali used in the titration of all runs up to and including Run 52 was 0.1094 N, while that used in all succeeding runs was 0.1165 N. The factors for calculating total mols of maleic acid from the number of ml. of alkali required to titrate a 10 ml. aliquot were derived as follows:

For 0.1094 N alkali: Factor = $\frac{0.1094 \times 24.92}{2 \times 1,000} = 0.001362$

For 0.1165 N alkali: Factor = $\frac{0.1165 \times 24.92}{2 \times 1,000} = 0.001452$

The factor 2 in the denominators of these expressions is required because maleic acid is dibasic.

In Table X are given the results from a preliminary run, and in Tables XI, XII, and XIII are given those from runs with pinene at optimum conditions, with dipentene, and with p-cymene, respectively. A porcelain filter crucible was used instead of the Gooch in the determinations listed in the last three tables. Hence instead of dissolving the precipitated barium salt and determining barium as $BaSO_4$, the crucible containing the salt was heated strongly over a Bunsen burner for half an hour whereby the barium maleate was converted to $BaCO_3$, which was weighed. During the heating the crucible was protected by a porcelain cup provided by the manufacturer for that purpose.

In applying the gravimetric method to the oxidation product the precision was somewhat less than when pure maleic acid was analyzed. This was undoubtedly due to the adsorption of foreign substances from the solution, as shown by the dark color of the precipitate. This accounts also for the low values for barium which were obtained under these conditions. In this connection it is interesting to note that yields of maleic acid calculated on the basis of the weight of $BaCO_3$ obtained agree more closely with the titrated values than the results calculated on the basis of the barium maleate. This may be due to the removal of adsorbed organic matter by the ignition, or it may be merely a fortuitous circumstance. In the absence of specific data it seems best to rely on the barium maleate monohydrate[25] the basis of the determination.

Table X. Comparison of Gravimetric and Volumetric Procedures For Maleic Acid.

Preliminary Run

Titration With 0.1094 N base

	Sample 1.	Sample 2.	Mean
Vol. of alkali for 10 ml Aliquot	19.60 m l.	19.60 ml.	19.60 ml.
Maleic acid by Titration	0.0267 mol.	0.0267 mol.	0.0267 mol.
$Ba.C_4H_2O_4.H_2O$ weighed	0.2787 g.	0.2860 g.	0.2824 g.
Maleic Acid, Gravimetric	0.0258 mol.	0.0265 mol.	0.0261 mol.
$BaSO_4$ weighed	0.2360 g.	0.2460 g.	0.2420 g.
Ba in $Ba.C_4H_2O_4.H_2O$	50.3%	50.6%	50.4%

Calculated for $BaC_4H_2O_4.H_2O$: Ba = 50.9%

Table XI. Comparison of Fravimetric and Volumetric Procedures For Maleic Acid.

Runs With Pinene At Optimum Conditions

Run 64. Pinene Oxidised: 0.0607 mol.

	Sample 1.	Sample 2.	Mean
Vol. Alkali for 10 ml. Aliquot	11.62 ml.	11.64 ml.	
Maleic Acid yield by Titration	27.8%	27.8%	27.8%
$Ba.C_4H_2O_4.H_2O$ weighed	0.4732 g.	0.4663 g.	
Maleic acid yield gravimetric	28.8%	28.4%	28.6%
$BaCO_3$ weighed	0.3395 g.	0.3350 g.	
Ba in $Ba.C_4H_2O_4.H_2O$	50.0%	50.0%	50.0%
Yield based on $BaCO_3$	28.8%	28.0%	28.2%

Run 65. Pinene Oxidised: 0.0827 mol.

	Sample 1.	Sample 2.	Mean
Vol. of alkali for 10 ml. aliquot	15.95 ml.	15.98 ml.	
Maleic acid yield by titration	28.1%	28.1%	28.1%
$Ba.C_4H_2O_4.H_2O$ weighed	0.6741 g.	0.6522 g.	
Maleic acid yield, gravimetric	29.0%	28.3%	28.6%
$BaCO_3$ weighed	0.4700 g.	0.4582 g.	
Ba in $Ba.C_4H_2O_4.H_2O$	50.0%	50.4%	50.4%
Yield based on $BaCO_3$	28.8%	28.1%	28.4%

Note: Titrations were made with 0.1185 N alkali.

Table XII. Comparison of Gravimetric and Volumetric Methods For Maleic Acid.

Runs With Dipentene.

Run 66. Dipentene Oxidized: 0.0515 mol.

	Sample 1.	Sample 2.	Mean
Vol. of alkali for 10 ml. aliquot	9.60 ml.	9.64 ml.	
Maleic acid yield by titration	27.0 %	27.2 %	27.1 %
$Ba.C_4H_2O_4.H_2O$ weighed	0.3903 g.	0.3808 g.	
Maleic acid yield gravimetric	28.0 %	27.4 %	27.7 %
$BaCO_3$ weighed	0.2805 g.	0.2747 g.	
Ba in $Ba.C_4H_2O_4.H_2O$	50.0 %	50.2 %	50.1 %
Yield based on $BaCO_3$	27.6 %	27.0 %	27.3 %

Run 67. Dipentene Oxidized: 0.0412 mol.

	Sample 1.	Sample 2.	Mean
Vol of alkali for 10 ml. aliquot	7.68	7.61	
Maleic acid yield by titration	27.1 %	26.8 %	26.9 %
$Ba.C_4H_2O_4.H_2O$ weighed	0.3102 g.	0.3028 g.	
Maleic acid yield gravimetric	27.9 %	27.2 %	27.6 %
$BaCO_3$ weighed	0.2218 g.	0.2195 g.	
Ba in $Ba.C_4H_2O_4.H_2O$	49.8 %	50.5 %	50.2 %
Yield based on $BaCO_3$	27.3 %	27.0 %	27.2 %

Note: Titrations were made with 0.1185 N alkali.

Table XIII. Comparison of Gravimetric And Volumetric Procedures For Maleic Acid.

Runs With p-Cymene.

Run 68. p-Cymene Oxidized: 0.0474 Mol.

	Sample 1.	Sample 2.	Mean
Vol. of Alkali for 10 ml. Aliquot	8.80 ml.	8.79 ml.	
Maleic Acid Yield By Titration	27.0 %	27.0 %	27.0 %
$Ba_2C_4H_2O_4.H_2O$ weighed	0.3478 g.	0.3528 g.	
Maleic Acid Yield, Gravimetric	27.1 %	27.5 %	27.3 %
$BaCO_3$ Weighed	0.2504 g.	0.2523 g.	
Ba In $Ba.C_4H_2O_4.H_2O$	50.2 %	49.8 %	50.0 %
Yield Based on $BaCO_3$	26.8 %	27.2 %	27.0 %

Run 69. p-Cymene Oxidized: 0.0392 Mol.

	Sample 1.	Sample 2.	Mean
Vol. Of Alkali For 10 ml. Aliquot	7.54 ml.	7.46 ml.	
Maleic Acid Yield By Titration	28.0 %	27.6 %	27.8 %
$Ba.C_4H_2O_4.H_2O$ Weighed	0.2861 g.	0.3009 g.	
Maleic Acid Yield, Gravimetric	28.0 %	28.4 %	28.2 %
$BaCO_3$ Weighed	0.2145 g.	0.2154 g.	
Ba In $Ba.C_4H_2O_4.H_2O$	50.4 %	49.8 %	50.1 %
Yield Based On $BaCO_3$	27.7 %	27.8 %	27.8 %

Note: Titrations were made with 0.1165 N alkali.

Aldehydes.— That aldehydes were formed in the oxidation was shown by the ability of the scrubber solution to restore the color to Schiff's Aldehyde reagent, and by its ability to reduce Tollen's ammoniacal silver nitrate solution. The odor of the solution suggested formaldehyde, and this was confirmed by the preparation of a semicarbazone, which melted at 166-8° C.

In those runs in which a heavy fog was produced, passage of the exit gas through an aldehyde reagent suggested by Mr. F. G. Singleton (77) of this laboratory, showed the presence of aromatic aldehydes. The reagent was N,N dibenzyl metaphenylenediamine, which reacts with aldehydes to give triphenylmethane derivatives. The aromatic compounds so formed become highly fluorescent after standing for some time, and hence the reagent is useful in distinguishing aromatic aldehydes from other types.

Some of the fog was collected as previously described, and yielded a 2,4-dinitrophenylhydrazone which showed the presence of toluic aldehyde.

Melting Point of Unknown 2,4-dinitrophenylhydrazone ..... 253-6° C.

Melting Point of authentic toluic aldehyde derivative .... 255-6° C.

Melting Point of Mixture ..... 253-6° C.

An attempt was made to determine aldehydes quantitatively by the peroxide method of Kolthoff and Furman (78). This consisted in oxidizing the aldehyde to acid by means of hydrogen peroxide in the presence of excess standard alkali, and back titrating the excess. The following procedure was used: A 10 ml. or 25 ml. aliquot was measured into a 250 ml. Erlenmeyer flask to which had previously been added 50 ml. of 0.1 N alkali and 50 ml. of 3% hydrogen peroxide, both accurately measured. The flask was closed with a rubber stopper carrying a soda-lime tube to protect it from

CO_2, and was was warmed for half an hour in a water bath. After cooling, phenolphthalein was added and the excess alkali titrated with standard acid. The peroxide was slightly acid, and hence a blank was run in the same manner. A similar sample was titrated for maleic acid and the appropriate correction made. In calculating aldehyde, each mol of alkali required above that required by the blank and the acid previously present corresponds to one mol of aldehyde.

The results obtained with this method were not entirely satisfactory. Checks between duplicate determinations often were poor, and the amounts of aldehyde indicated in a number of runs do not show any definite trends. In view of the uncertainties involved in applying a reagent like H_2O_2 to an unknown solution, it is doubtful if any great significance can be attached to the results. However, the values obtained are listed in the tables of data.

Gas Analysis:— Gas analyses were made only in the final runs with pinene, and in those with dipentene and p-cymene. The standard Orsat method was used, with KOH solution for absorption of CO_2, sodium pyrogallate for absorption of oxygen, acid cuprous chloride for CO, and fuming sulfuric acid for olefins. Samples were drawn directly from a tee on the exit line into the gas analysis apparatus. Determinations were made at intervals during a run, and the mean values used in the calculations. No olefins were detected, and surprisingly no CO was found. Even bubbling the exit gas through palladous chloride solution, a delicate reagent, failed to show a trace of CO.

Calculations.

In order to illustrate the method of calculating results, the complete figures for Run 65, in which pinene was oxidized at optimum conditions, are given. By direct measurement, the following data were available:

Temperature of carburetor thermostat	28.7°	C.
Weight of carburetor before run	188.00	g.
Weight of carburetor after run	176.75	g.
Weight of pinene oxidized (by difference)	11.25	g.
Time at which run was started	11:15	a.m.
Time at which run was completed	9:15	p.m.
Duration of run (by difference)	600	min.
Reading of primary flowmeter (orifice No. 1)	51.8	
Rate of flow of primary air (Fig. 2)	0.49	l./min.
Reading of secondary flowmeter	25.6	
Rate of flow of secondary air (Fig. 2)	1.48	l./min.
Total rate of flow (primary + secondary air)	1.97	l./min.
Average room temperature at which air was measured	31°	C.
Average pyrometer reading	500	
Average reaction temperature (Fig. 4)	426°	C.
Total volume of catalyst	16.6	ml.
Free volume of catalyst space (60% of total)	9.96	ml.
Oxygen in exit gas	20.0	%
CO_2 in exit gas	0.7	%
Nitrogen in exit gas (by difference)	79.3	%
Titer of 10 ml. aliquot of product (0.1165 N alkali)	15.98	ml.
Total alkali aldehyde determination (10 ml. aliq.) 1.	50.05	ml.
2.	49.98	ml.
Back titration (0.0969 N acid) 1.	15.55	ml.
2.	15.49	ml.
Blank titration on peroxide	2.96	ml.

C alculations were made from these data as described below.

1. Contact Time.-- In view of the discussion in the Introduction, it is apparent that pinene alone, if passed through the reactor would undergo a complicated series of reactions, possibly involving an increase in the number of molecules present. Add to this the manifold changes brought about by interaction between the pinene and oxygen, and it is obvious that

to calculate accurately the volume of gas passing through the catalyst zone was impossible. However, the process was operated with large amounts of diluent gases which did not take part in the reaction. Therefore the percentage change in the total number of mols present, due to reaction occuring in the catalyst zone, was relatively small. Consequently, a figure which represented at least the order of magnitude of the time of contact was calculated on the basis of the number of mols of material entering the catalyst zone, the duration of the run, the catalyst temperature, and the net or free volume of the catalyst space. By time of contact is meant the time required for the reacting gasses to pass through the catalyst. It w as calculated as follows:

Temperature at which air was measured = 31 + 273 =..... 304° K.

Temperature of reaction = 426 + 273 =..... 699° K.

Total volume of air at 31° C. = 600 X 1.97 = ... 1182 l.

Total volume of air at 426° C. = $\frac{1182 \times 699}{304}$ = ... 2718 l.

Volume of pinene vapor at 426° C. = $\frac{0.0827 \times 22.4 \times 699}{273}$,

which simplifies to: 0.0827 X 0.082 X 699 = 5 l.

Total volume of reacting gases = 2718 + 5 = ... 2723 l.

Contact time = $\frac{9.96 \times 600 \times 60}{1,000 \times 2723}$,

which simplifies to: $\frac{0.598 \times 600}{2723}$ = ... 0.13 sec.

Contact time, therevore, was calculated by means of the expression:

$$\text{Contact time} = \frac{0.598 \times (\text{duration of run})}{(\text{gas vol at reaction temp.})}$$

2. Space Velocity.— A better measure of the rate factor is given by the space velocity, which is defined as the number of liters of reacting gases (measured at Standard Conditions) which are passed per hour per liter of catalyst space. It was calculated as follows:

Temperature at which air was measured..... 304° K.

Volume of air at this temperature..... 1182 l.

Volume of air at 0° C. = $\frac{1182 \times 273}{304}$ = ... 1061 l.

Mols of pinene oxidized..... 0.0827 mol

Volume of pinene vapor at 0° C. = 0.0827 X 22.4 = 2 l.

Total volume of reacting gases at 0° C. = 1061 + 2 = ... 1063 l.

Space velocity = $\frac{1063 \times 1,000 \times 60}{600 \times 16.6}$ = ... 6400 l/hr.

Space velocity, therefore, was calculated by means of the expression:

$$\text{Space velocity} = \frac{3614 \times (\text{gas vol. at S.C.})}{(\text{duration of run})}$$

3. Mol ratio of Oxygen to Pinene.— Since oxygen is the active constituent of the air it was deemed better to consider the amount of pinene reacting relative to oxygen rather than to the total mols of gas. The two values of course are proportional. In making the calculation, it was assumed that air contains 20.7 % oxygen.

Temperature at which air was measured..... 304° K.

Volume of air at this temperature..... 1182 l.

Mols of oxygen in air = $\frac{1182 \times 0.207 \times 273}{22.4 \times 304}$, =

which simplifies to: $\frac{1182 \times 2.52}{304}$ = ... 9.80 mols

Mols of pinene reacted..... 0.0827 mol

Ratio, mols oxygen : mols pinene = $\frac{9.80}{0.0827}$ = ... 118

Mols of oxygen in air feed, then is given by:

$$\text{Mols oxygen in air} = \frac{(\text{measured vol. of air}) \times 2.52}{(\text{temp. at which measured})}$$

4. Total CO_2 Produced.— It has already been mentioned that no CO or olefins were found in the exit gas, and from a comparison of the composition of the spent gas with that of the original air, it was concluded that the exit gas consisted essentially of N_2, O_2, and CO_2. From the equation for the formation of CO_2

$$C + O_2 = CO_2$$

it is apparent that one mol of O_2 gives rise to one mol of CO_2. Hence, in calculating the total CO_2 produced it was assumed that the CO_2 found had replaced its own volume of O_2 in the original air, and that the spent gas had the same volume as the original air. This is subject to a slight error because of oxygen used in the production of oxygenated organic compounds.

Volume of air at 0° C. ..... 1061 l.

Mols of CO_2 = $\frac{1061 \times 0.007}{22.4}$ = ... 0.332 mol

5. Maleic Acid Yield.— The method of calculation of total maleic acid from the titer of an aliquot of the product has been given in the section dealing with analysis of product. For Run 65:

Titer ..... 15.98 ml.

Mols of maleic ac id = 15.98 X 0.001452 = ... 0.0232 mol

Mols of pinene oxidized ..... 0.0827 mol

Maleic acid yield = $\frac{0.0232}{0.0827}$ = ... 28.1 %

6. Aldehyde Yield.— The analytical method which was used did not distinguish between formaldehyde and other members of this class, but since formaldehyde was shown to be the principal aldehyde formed, and since any appreciable amount of aromatic aldehydes would betray their presence by separating from the solution, it was assumed that the data given by the analysis represented formaldehyde.

	1.	2.
Blank titration on peroxide	2.96 ml.	2.96 ml.
Titer of acids in solution	15.98 ml.	15.98 ml.
Alkali equivalent of back titration	12.92 ml.	12.89 m l.
Total excess alkali	31.86 ml.	31.83 ml.
Total alkali added	50.05 ml.	49.98 ml.
Alkali equivalent to aldehyde	18.17 ml.	18.15 ml.
Mean		18.16 ml.

$$\text{Total mols aldehyde} = \frac{18.16 \times 0.1165 \times 24.92}{1{,}000},$$

which simplifies to: $18.16 \times 0.00290 = 0.0527$ mol.

Assuming that each molecule of pinene yields one molecule of formaldehyde, the yield is:

$$\frac{0.0527}{0.0827} = \ldots\ldots\ldots\ldots\ 63.7\ \%$$

Experimental Results

Direct measurements for all runs are collected in Table XIII, and data calculated from these measurements are presented in the tables and curves which follow. The first column of Table XIII gives the run number. The second column, headed Room Temperature, gives the temperature at which the air was measured. The third column, headed Bath Temperature, gives the temperature of the thermostat in which the carburetor was immersed. The fourth column, headed Catalyst Temperature, gives the temperature of the salt bath surrounding the catalyst tube. Column 5 gives the duration of the run in minutes. Column 6 gives the rate of flow of air through the carburetor, measured in liters per minute by meter No. 1. Columns 7 and 8 give the rate of flow of secondary air, measured in liters per minute by meters No.2 and No.3 respectively. Column 9 gives the weight in grams of hydrocarbon fed to the reactor.

Column 10 gives the volume of alkali required to titrate the maleic acid in a 10 ml. aliquot of the product. Column 11 gives the net volume of alkali, corrected for maleic acid, blank titration and back titration, equivalent to the aldehyde in an aliquot of the product. The aldehyde determination in Runs 19 thru 65 was made on a 10 ml. aliquot, while that in Runs 66 thru 69 was made on a 25 ml. aliquot. It should be noted also that the normalities of the alkali and acid used were not the same in all runs. Analyses in Runs 1 thru 32 were made with:

Table XIII. Primary Measurements For All Runs.

Run No.	Temperature. Room °C.	Bath °C.	Catalyst °C.	Time Min.	Rate of Air Flow Pri. No.1 l/m	Sec. No.2 l/m	Sec. No.3 l/m	Feed g.	Titration Acid ml.	Ald. ml.	CO_2 in Exit Gas %	Unreacted g.
1	30	60.5	386	218	1.38	1.55	—	60.50	38.60	—	—	9.5
2	31	60.5	410	208	1.37	1.55	—	59.50	46.10	—	—	—
3	31	60.5	435	213	1.37	1.55	—	59.50	45.70	—	—	—
4	31	60.5	452	185	1.37	1.55	—	50.80	38.80	—	—	—
5	28	71.0	383	129	1.38	1.76	1.72	57.80	6.00	—	—	21.2
6	28	72.0	416	125	1.37	1.74	1.68	58.10	5.60	—	—	—
7	31	53.0	386	260	1.39	0.61	—	52.40	9.50	—	—	—
14	23	51.0	464	135	0.36	0.84	—	9.65	10.56	—	—	—
19	23	55.0	463	437	0.60	—	—	14.85	15.96	19.30	—	—
20	24	35.0	465	440	0.87	—	—	21.45	25.10	21.85	—	—
21	22	55.0	463	270	1.30	—	—	21.60	21.89	24.20	—	—
22	21	56.0	463	540	0.51	—	—	9.55	8.44	14.55	—	—
23	21	55.0	400	300	1.38	—	—	25.80	7.60	21.61	—	5.6
24	20	55.0	400	280	0.87	—	—	12.60	4.99	15.23	—	1.6
25	22	55.0	400	480	0.51	—	—	8.55	9.54	14.05	—	0.5
26	22	55.0	435	480	0.51	—	—	8.40	9.46	9.65	—	tr.
27	24	55.0	435	240	0.87	—	—	12.70	14.40	19.71	—	—
28	24	54.5	435	210	1.38	—	—	18.85	18.00	28.35	—	—
29	22	54.5	515	240	1.38	—	—	19.30	16.20	18.17	—	—
30	22	54.5	515	320	0.87	—	—	15.65	12.22	—	—	—
31	25	54.5	515	420	0.69	0.69	—	15.70	13.58	25.29	—	—
32	25	54.5	463	420	0.69	0.69	—	14.85	16.04	25.51	—	—
33	25	54.5	435	375	0.69	0.69	—	13.10	16.01	—	—	—
34	25	54.5	400	360	0.69	0.69	—	11.85	12.00	—	—	tr.
35	23	54.7	515	420	0.44	0.45	—	8.95	6.56	—	—	—
36	29	54.7	463	420	0.44	0.45	—	10.60	11.49	—	—	—
37	24	55.0	435	420	0.44	0.45	—	10.40	11.05	—	—	—
38	20	55.0	400	420	0.44	0.45	—	10.10	9.51	—	—	—
39	24	55.0	515	215	1.41	1.40	—	17.70	18.14	—	—	—
40	25	55.0	463	180	1.41	1.40	—	14.20	15.87	—	—	—

Table XIII (Concluded). Primary Measurements For All Runs.

Run No.	Temperature			Time	Rate of Air Flow			Feed	Titration		CO_2 in Exit Gas	Unreacted
	Room	Bath	Catalyst		Pri.	Sec.			Acid	Ald.		
	°C	°C	°C	Min.	No.1 l/m	No.2 l/m	No.3 l/m	g.	ml.	ml.	%	g.
41	25	55.0	425	180	1.41	1.40	—	14.45	14.85	—	—	—
42	24	55.0	396	180	1.41	1.40	—	14.50	5.27	—	—	2.8
43	30	28.7	463	340	0.70	1.05	1.05	9.65	11.85	—	—	—
44	29	28.7	515	320	0.70	1.05	1.05	9.00	9.51	—	—	—
45	29	28.7	426	360	0.70	1.05	1.05	10.10	14.15	—	—	—
46	28	28.7	394	360	0.70	1.05	1.05	10.20	6.60	—	—	—
47	29	28.7	390	240	0.77	1.52	1.54	8.15	5.79	—	—	—
48	30	28.7	450	172	0.77	1.50	1.51	5.65	7.59	—	—	—
49	30	28.7	466	240	0.77	1.54	1.56	8.15	10.56	—	—	—
50	27	28.7	515	240	0.77	1.53	1.54	8.20	9.45	—	—	—
51	28	28.7	515	360	0.49	1.48	—	7.20	7.58	—	—	—
52	28	28.7	466	360	0.49	1.48	—	7.10	8.58	—	—	—
53	28	28.7	426	360	0.49	1.48	—	7.15	10.60	—	—	—
54	28	28.7	394	240	0.49	1.48	—	4.85	4.43	—	—	—
55	28	28.7	426	240	1.05	0.87	0.87	9.70	13.02	—	—	—
56	28	28.7	466	240	1.05	0.87	0.87	9.55	11.88	—	—	—
57	30	28.7	426	420	0.55	1.05	—	6.75	9.16	—	—	—
58	28	28.7	467	420	0.55	1.05	—	5.75	5.98	—	—	—
59	30	28.7	390	420	0.35	1.05	—	5.85	5.80	—	—	—
62	32	28.7	430	468	0.44	1.52	—	8.55	11.12	18.62	—	—
63	32	28.7	428	720	0.26	0.86	0.86	6.80	10.00	—	—	—
64	35	28.7	426	450	0.49	1.48	—	8.25	11.63	13.72	0.7	—
65	31	28.7	426	600	0.49	1.48	—	11.25	15.96	18.18	0.7	—
66	31	28.7	426	420	1.04	0.94	—	7.00	9.62	32.91	0.6	—
67	29	28.7	430	360	1.09	0.88	—	5.60	7.94	26.59	0.6	—
68	28	28.7	426	420	1.10	0.89	—	6.35	8.80	33.00	0.5	—
69	31	29.0	426	360	1.10	0.89	—	5.25	7.50	27.86	0.5	—
71	31	31.0	464	200	0.36	0.84	—	9.67	9.80	—	—	—
72	30	31.0	425	220	0.93	1.07	—	24.65	19.94	—	—	—
73	30	28.7	515	420	0.35	1.05	—	5.80	4.85	—	—	—

Alkali 0.1094 N Acid 0.1056 N

Analyses in Runs 56 thru 75 were made with:

Alkali 0.1165 N Acid 0.0969 N.

Column 12 gives the CO_2 content of the exit gas. Oxygen content was not recorded, because it was found that the sum of the CO_2 and oxygen in the exit gas was equal to the oxygen in the original air, as previously explained.

In a few runs a liquid product insoluble in water was produced and separated from the scrubber solution. This was collected and weighed, and is reported in Column 13 as Unreacted. In those runs in which the amount was too small to be weighed, a trace is reported. Altho this substance was not thoroughly investigated, one sample obtained from a series of preliminary runs was fractionated, and the results indicated that it consisted principally of pinene and its isomeration products, and polymer. The results of the fractionation are given in Table XIV. For comparison, the boiling points of pinene and dipentene under the pressure used are also given. These were calculated from the equation of Rudakov and Koretov (78).

Table XIV. Fractionation of Water-Insoluble Liquid Product.

Pressure 36 mm of Hg.

Volume of Charge 160 ml.

Fraction	Volume, ml.	Boiling Range, °C.
1	75	65 - 70
2	28	70 - 80
3	19	80 - 84
4	14	84 - 88
5	4	88
Semi-solid residue	20 (by diff.)	
Pinene		65
Dipentene		84

It should be noted that Runs 1 through 7 were made with t three-tube reactor with a total catalyst volume of 61 cc. and a catalyst free volume of 36.6 cc. The remainder of the runs were made with a single-tube reactor with a total catalyst volume of 16.6 cc. and a catalyst free space of 9.96 cc.

All runs were made with pinene except Runs 66, 67, 68, and 69. Runs 66 and 67 were made with dipentene, and Runs 68 and 69 were made with p-cymene.

Effect of Reaction Temperature.— The data from a number of runs have been arranged in groups according to oxygen-pinene ratio, and these have been divided into subgroups according to space velocity. Finally the individual runs have been arranged in the subgroups in the order of increasing temperature. In this way Tables XV, XVI and XVII were constructed, and from these the curves in Figs. 5, 6 and 7 were plotted, showing maleic acid yield as a function of temperature.

The curves of Figs. 5, 6 and 7 show that under all the conditions studied there is an optimum temperature at which maleic acid formation reaches a maximum. Below this temperature the yield falls off rapidly, presumably because a smaller proportion of the pinene is attacked by oxygen. The principal reaction under these conditions probably is isomerization of pinene. Above the optimum temperature the yield gradually falls, as a result of the complete combustion of an increasing proportion of the pinene. The temperature of maximum yield lies between 420 and 450° C ., and the position of the maximum varies with space velocity and

oxygen-pinene ratio, as will be seen later.

Effect of Space Velocity.-- Values of space velocity and temperature were not duplicated exactly in the various groups of runs. Hence it was necessary to read corresponding values of yield and space velocity at fixed temperatures from the curves of Figs. 5, 6, and 7. These are listed in Table XVIII, XIX and XX. The data for runs with an oxygen-pinene ratio of 20 are inconclusive, and therefore were not plotted. Data at ratios of 42 and 113 were plotted, and appear in Fig. 8 and 9.

The form of the yield-space velocity curves is in general similar to that of the yield-temperature curves, that is, they show an optimum space velocity at which maximum yield occurs. Apparently, at low space velocity the reacting gases remain in contact with the catalyst long enough for considerable combustion to occur, while at high velocities the time of contact is insufficient for the formation of optimum yields of maleic acid.

Table XV. Maleic Acid Yield Versus Temperature.

Average mol ratio of oxygen to pinene = 20

Run No.	Mol Ratio O_2:Pinene	Space Velocity 1/hr	Contact Time Sec.	Unreacted %	Aldehyde Yield %	Maleic Acid %	Temp. °C.
25	20.2	1050	0.84	5.8	60.7	20.6	400
26	20.5	1050	0.80	tr.	42.5	20.8	435
22	20.4	1050	0.76	—	55.5	16.3	465
24	21.0	2980	0.30	12.3	44.7	7.3	400
27	19.0	2930	0.29	—	57.5	21.0	435
20	21.1	2930	0.27	—	39.4	12.9	465
30	20.6	2930	0.26	—	—	14.5	515
23	20.3	4680	0.19	23.5	32.0	5.9	400
28	19.8	4630	0.18	—	64.5	19.8	435
21	18.9	4670	0.18	—	42.4	19.0	465
29	19.9	4660	0.18	—	36.8	15.6	515

Table XVI. Maleic Acid Yield Versus Temperature.

Average mol ratio of oxygen to pinene = 42

Run No.	Mol Ratio O_2:Pinene	Space Velocity 1/hr	Contact Time Sec.	Unreacted %	Maleic Acid %	Temp. °C.
38	43.3	3010	0.29	tr.	18.2	400
37	41.4	2970	0.28	tr.	21.0	435
36	40.0	2920	0.27	—	17.2	465
35	42.0	2980	0.25	—	14.5	515
34	45.0	4620	0.19	tr.	20.0	400
33	45.5	4590	0.18	tr.	24.1	435
32	45.2	4620	0.17	—	20.0	465
31	45.0	4590	0.16	—	16.9	515
42	40.2	9560	0.09	20.7	7.2	396
41	40.3	9560	0.09	tr.	20.3	423
40	40.9	9550	0.09	—	22.1	463
39	39.4	9 560	0.08	—	20.2	515

Table XVII. Maleic Acid Yield Versus Temperature.

Average mol ratio of oxygen to pinene = 113.

Run No.	Mol Ratio O_2:Pinene	Space Velocity l/hr	Contact Time, Sec.	Maleic Acid %	Temperature °C.
59	115.9	4570	0.19	12.8	390
57	110.0	4570	0.18	26.8	426
58	113.3	4600	0.17	20.5	467
73	114.4	4570	0.16	16.8	515
54	110.9	6470	0.14	18.0	394
55	111.6	6470	0.13	29.5	428
52	113.8	6470	0.12	25.3	466
51	112.3	6470	0.12	20.8	515
46	112.5	9200	0.10	12.8	394
45	113.2	9170	0.09	27.6	428
43	111.5	9140	0.09	24.2	465
44	113.0	9170	0.08	20.9	515
47	114.7	11200	0.08	14.0	390
48	113.6	11000	0.08	25.4	430
49	115.7	11200	0.07	25.6	466
50	115.1	11500	0.07	22.8	515

Table XVIII. Maleic Acid Yield Versus Space Velocity.

Average mol ratio of oxygen to pinene = 20

Temperature °C.	Space Velocity l/hr	Maleic Acid %
400	1050	20.6
400	2900	7.3
400	4660	5.8
425	1050	21.0
425	2900	20.2
425	4660	19.1
425	6570	16.0
460	1050	16.9
460	2900	20.1
460	4660	19.1
500	2900	16.5
500	4660	16.7

Table XII. Maleic Acid Yield Versus Space Velocity

Average mol ratio of oxygen to pinene = 42

Temperature °C.	Space Velocity l/hr	Maleic Acid %
400	2970	18.2
400	4600	20.0
400	9370	10.5
425	2970	21.5
425	4600	24.0
425	9370	20.8
500	2900	14.8
500	4600	17.2
500	9370	20.5

Table XX. Maleic Acid Yield Versus Space Velocity.

Average Mol ratio of oxygen to pinene = 115.

Temperature °C.	Space Velocity l/hr	Maleic Acid %
400	4,580	20.9
400	6,470	23.4
400	9,170	19.3
400	11,200	18.9
425	4,580	28.9
425	6,470	29.5
425	9,170	27.6
425	11,200	24.9
450	4,580	25.2
450	6,470	25.6
450	9,170	25.8
450	11,200	26.2
500	4,580	17.5
500	6,470	21.2
500	9,170	21.6
500	11,200	23.4

As would be expected, the values of space velocity which give maximum yields are greatly influenced by the catalyst temperature. Increasing the temperature increases the velocity required for maximum yield. This is undoubtedly caused by the increased reaction rate resulting from the higher temperature, and the consequent necessity of removing the reacting gas mixture from the catalyst more quickly. The optimum space velocities at various temperatures and the corresponding yields, taken from the curves of Figs 8 and 9, are collected in Table XXI. It will be noted that optimum space velocities were not reached at the higher temperatures. The trend in yields did not indicate that investigation of this range would be fruitful.

Variation of space velocity also shifts the peaks on the yield-temperature curves. The effect is small, however, as shown by the data in Table XXII. These data were taken from the curves in Fig 5, 6 and 7.

Table XII. Effect of Temperature on Optimum Space Velocity.

Oxygen-Pinene Ratio	Temp. °C.	Optimum Space Velocity l/hr	Maximum Yield %
42	400	4500	20.0
42	425	5400	24.5
42	500	Above 10,000	Not Reached
115	400	6600	25.4
115	425	6850	29.5
115	450	Above 12,000	Not Reached
115	500	Above 12,000	Not Reached

Table XIII. Effect of Space Velocity on Optimum Temperature.

Oxygen-Pinene Ratio	Space Velocity l/hr	Optimum Temp. °C.	Maximum Yield %
20	1,050	422	21.1
20	2,900	435	21.1
20	4,860	458	19.6
42	2,970	425	21.5
42	4,600	435	24.2
42	9,570	448	22.8
115	4,580	425	26.9
115	6,470	425	29.5
115	9,170	425	27.6
115	11,200	452	26.2

Effect of Oxygen-Pinene Ratio.— The oxidation of a mole of pinene to maleic acid requires 11 mols of gaseous oxygen, as shown by the following equation:

$$C_{10}H_{16} + 11O_2 = C_4H_4O_4 + 6CO_2 + 6H_2O$$

Accordingly, in the first runs, air and pinene were fed at such a rate as to give a ratio of oxygen to pinene of approximately 11. After these runs were completed the catalyst was examined, and it was found that partial fusion had occurred. This indicated that at this ratio, local temperatures of at least 800° C., the fusion point of V_2O_5, had developed in the catalyst. This undoubtedly accounts for the low yields obtained under these conditions. Data for runs with an oxygen-pinene ratio of 11 are listed in Table XXIII.

Table XXIII. Runs at Theoretical Oxygen-Pinene Ratio.

Run No.	O_2-Pinene Ratio	Temp. °C.	Space Velocity	Contact time Sec.	Maleic Acid Yield %.
1	11.6	386	2850	0.35	11.8
2	11.5	410	2810	0.35	14.4
3	11.7	435	2810	0.32	14.0
4	11.9	452	2810	0.31	14.1
5	12.3	383	4400	0.20	2.6
6	11.6	416	4380	0.20	1.2
7	10.6	386	1710	0.52	5.4

The experiments just described indicated that greater dilution of the reacting gases was necessary in order to obtain good yields of maleic acid. Therefore, groups of runs were made with oxygen-pinene ratios of

20, 42, 80, 113 and 220. Data at ratios of 20, 40 and 113 have already been presented, and are found in Tables XV, XVI and XVII. The additional data are listed in Table XXIV.

Table XXIV. Additional Data On Oxygen-Pinene Ratio.

Run No.	O_2-Pinene Ratio	Temp. °C.	Space Velocity 1/hr.	Contact Time Sec.	Maleic Acid Yield %.
72	20.2	425	6570	0.13	18.0
55	79.8	426	9180	0.09	26.5
56	80.2	406	9180	0.09	24.2
63	220	426	6510	0.13	29.0

These data, together with values read from the curves of figs 8 and 9 are summarized in Table XXV, showing the relation between Maleic acid yield and oxygen-pinene ratio. The data are plotted in Fig. 10. It is evident from Fig. 10 that at a temperature of 425° C. and a space velocity of 6510, the yield increases rapidly with oxygen-pinene ratio until a value of approximately 100 is reached. Beyond this point no further increase occurs.

Table XX V. Oxygen-Pinene Ratio Versus Maleic Acid Yield.

Space Velocity 1/hr.	Oxygen-Pinene Ratio	Maleic Acid Yield %
6510	20	18.0
6510	42	23.9
6510	113	29.3
6510	220	29.0
9180	42	20.9
9180	80	26.5
9180	113	27.4

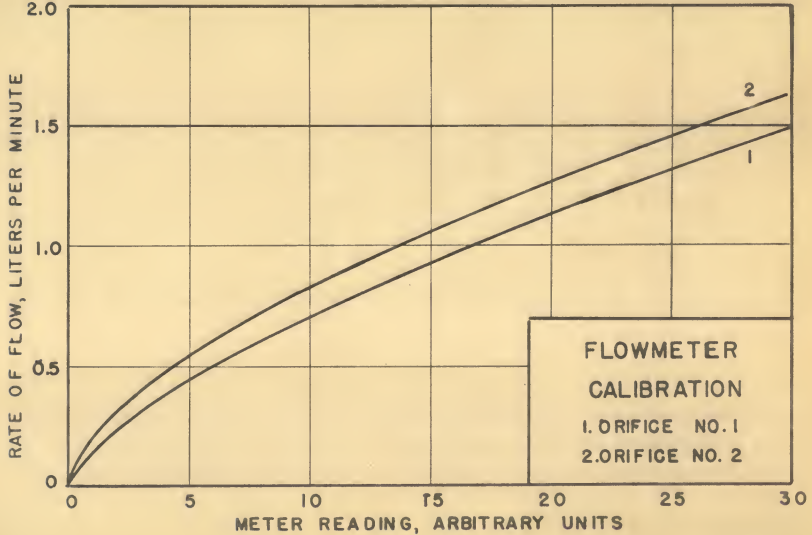
2.0
1.5
1.0
0.5
0
RATE OF FLOW, LITERS PER MINUTE
0
5
10
15
20
25
30
METER READING, ARBITRARY UNITS
2
1
FLOWMETER
CALIBRATION
1. ORIFICE NO. 1
2. ORIFICE NO. 2

Fig. 2.

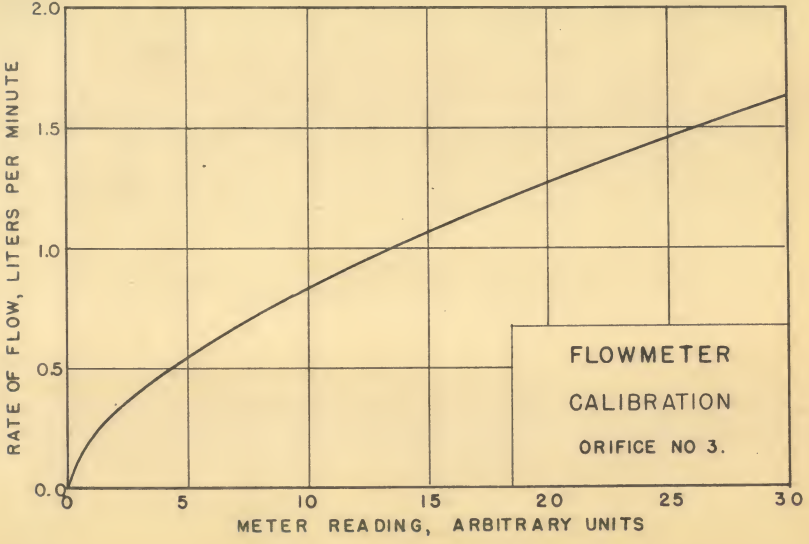
2.0
1.5
1.0
0.5
0.0
RATE OF FLOW, LITERS PER MINUTE
0
5
10
15
20
25
30
METER READING, ARBITRARY UNITS
FLOWMETER
CALIBRATION
ORIFICE NO 3.

Fig. 3.

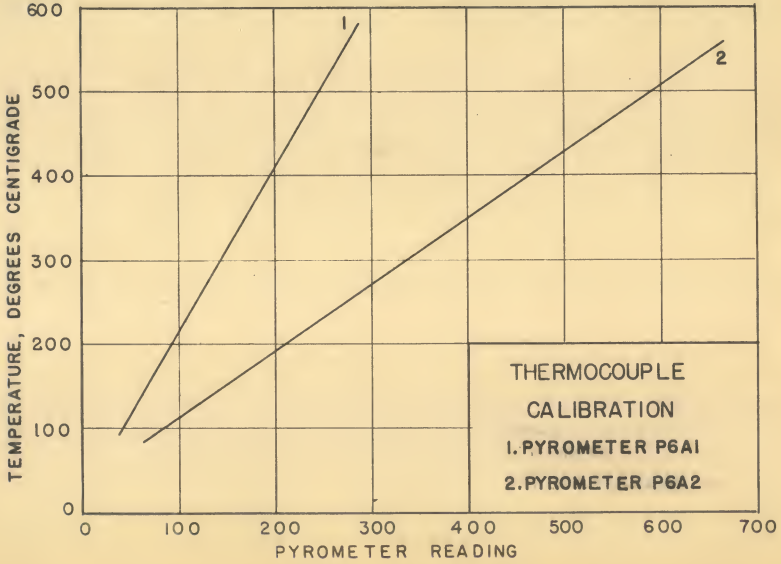
600
500
400
300
200
100
0
TEMPERATURE, DEGREES CENTIGRADE
0
100
200
300
400
500
600
700
PYROMETER READING
1
2
THERMOCOUPLE
CALIBRATION
1. PYROMETER P6A1
2. PYROMETER P6A2

Fig. 4.

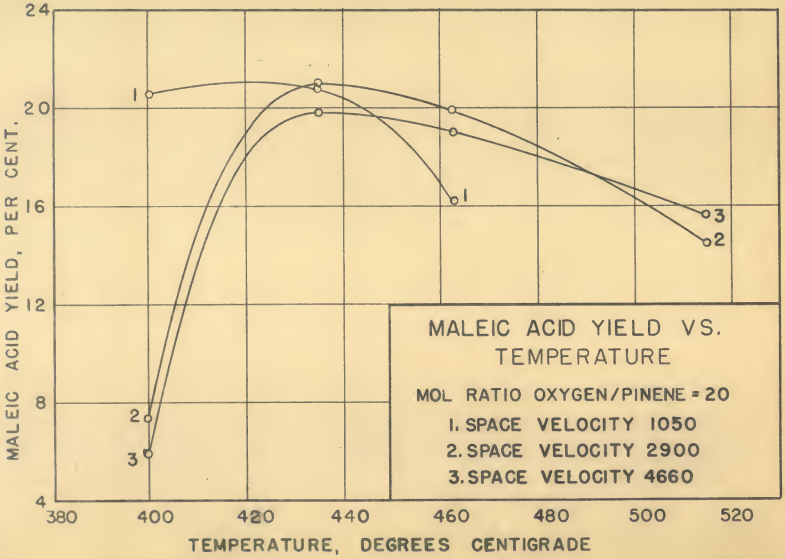
MALEIC ACID YIELD VS. TEMPERATURE
MOL RATIO OXYGEN/PINENE = 20
1. SPACE VELOCITY 1050
2. SPACE VELOCITY 2900
3. SPACE VELOCITY 4660
MALEIC ACID YIELD, PER CENT.
TEMPERATURE, DEGREES CENTIGRADE
24
20
16
12
8
4
380
400
420
440
460
480
500
520
1
2
3

Fig. 5.

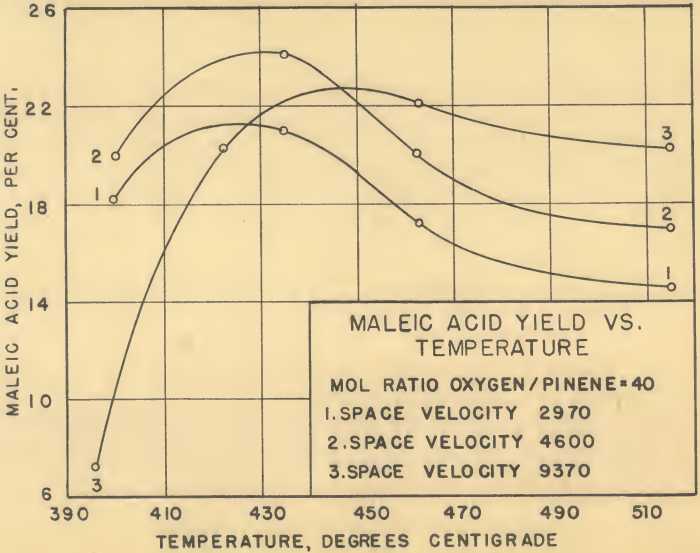
MALEIC ACID YIELD, PER CENT.
26
22
18
14
10
6
390
410
430
450
470
490
510
TEMPERATURE, DEGREES CENTIGRADE
MALEIC ACID YIELD VS. TEMPERATURE
MOL RATIO OXYGEN/PINENE=40
1. SPACE VELOCITY 2970
2. SPACE VELOCITY 4600
3. SPACE VELOCITY 9370
1
2
3

Fig. 6.

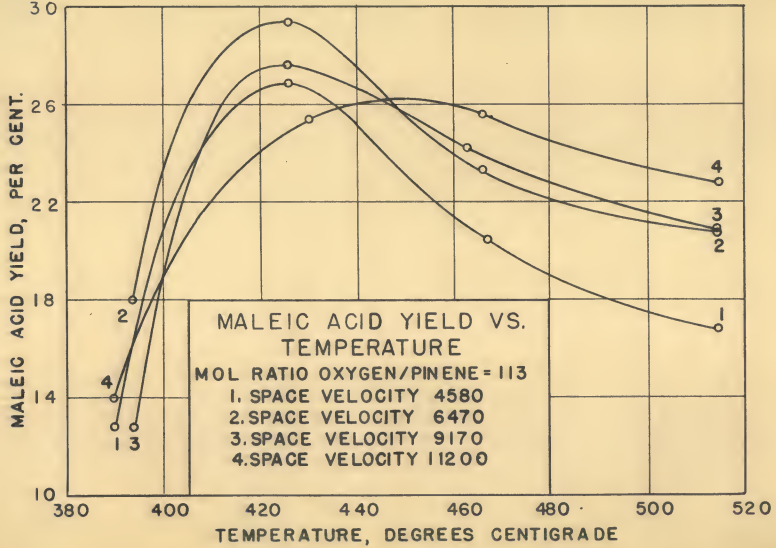
MALEIC ACID YIELD VS. TEMPERATURE
MOL RATIO OXYGEN/PINENE = 1:3
1. SPACE VELOCITY 4580
2. SPACE VELOCITY 6470
3. SPACE VELOCITY 9170
4. SPACE VELOCITY 11200
MALEIC ACID YIELD, PER CENT.
TEMPERATURE, DEGREES CENTIGRADE
30
26
22
18
14
10
380
400
420
440
460
480
500
520

Fig. 7.

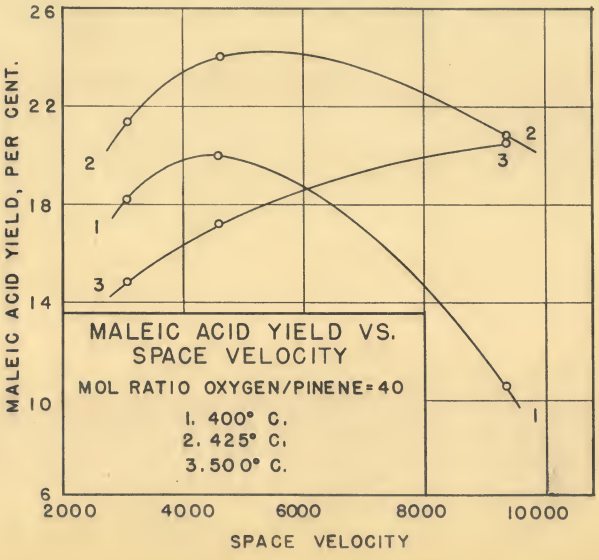
MALEIC ACID YIELD, PER CENT.
26
22
18
14
10
6
2000
4000
6000
8000
10000
SPACE VELOCITY
MALEIC ACID YIELD VS. SPACE VELOCITY
MOL RATIO OXYGEN/PINENE=40
1. 400° C.
2. 425° C.
3. 500° C.
1
2
3

Fig. 8.

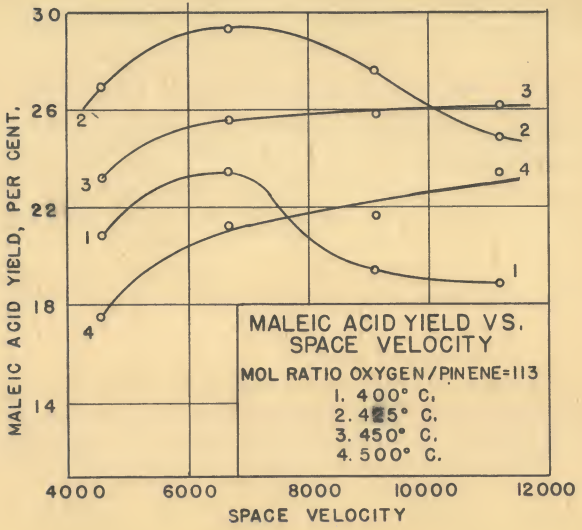
30
26
22
18
14
MALEIC ACID YIELD, PER CENT.
4000
6000
8000
10000
12000
SPACE VELOCITY
MALEIC ACID YIELD VS. SPACE VELOCITY
MOL RATIO OXYGEN/PINENE=113
1. 400° C.
2. 425° C.
3. 450° C.
4. 500° C.
1
2
3
4

Fig. 9.

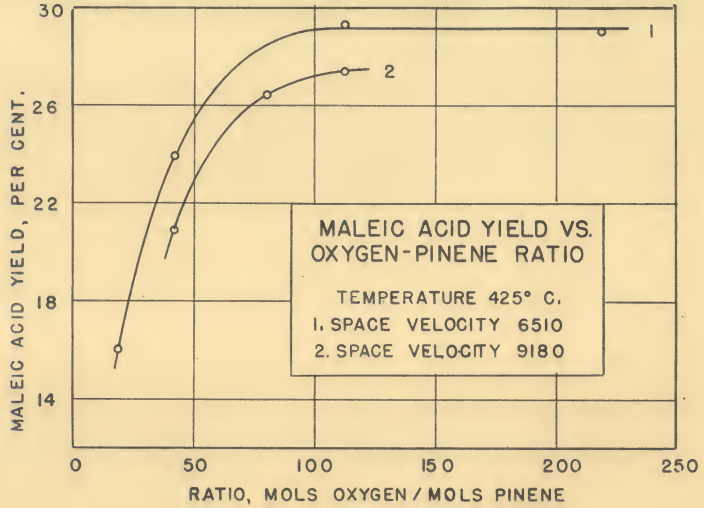
MALEIC ACID YIELD VS.
OXYGEN-PINENE RATIO
TEMPERATURE 425° C.
1. SPACE VELOCITY 6510
2. SPACE VELOCITY 9180
MALEIC ACID YIELD, PER CENT.
30
26
22
18
14
0
50
100
150
200
250
RATIO, MOLS OXYGEN / MOLS PINENE
1
2

Fig. 10.

Conditions For Maximum Yield.— This study indicates that with the particular catalyst and reactor used, maximum yields of maleic acid were obtained under the following conditions:

Diameter of catalyst tube	1.5 cm.
Length of catalyst zone	12.5 cm.
Total volume of catalyst zone	13.6 cc.
Free volume of catalyst	9.96 cc.
Catalyst support	3mm. pumice.
Active catalyst	V_2O_5
Reactor Bath Temperature	425° C.
Space velocity	6500 l/hr.
Mol ratio of Oxygen to pinene	100
Maximum yield of maleic acid	29 %

Oxidation of Dipentene and p-Cymene.— As pointed out in the Introduction, pinene is readily isomerized by heat to dipentene. Dipentene, in turn, can be dehydrogenated to p-cymene by the action of mild oxidising agents such as sulfur and selenium. Therefore, in an oxidizing atmosphere at high temperature, such as exists in the oxidation experiments, the formation of dipentene and p-cymene is probable. Furthermore, if these compounds are intermediates in the oxidation of pinene, they might be expected to behave similarly to pinene if passed through the reactor under similar conditions.

To provide data on this point the runs listed in Table XXVI were carried out. It is evident that practically identical results were obtained

when pinene, dipentene and p-cymene were oxidized under similar conditions. While such evidence is not conclusive, it indicated that dipentene and p-cymene may occur as intermediates in the oxidation of pinene to maleic acid.

Table XXVI. Comparison of Pinene, Dipentene and p-Cymene.

Temperature 426° C.

Run No.	Compound Oxidized	O_2-Hydrocarbon Ratio	Space Velocity	Mols of Product Per Mol of Hydrocarbon		
				Aldehyde	Maleic Acid	CO_2
64	Pinene	115	6360	0.656	0.278	3.89
65	Pinene	118	6400	0.637	0.281	4.01
66	Dipentene	134	6440	0.742	0.271	3.88
67	Dipentene	144	6440	0.749	0.269	4.17
68	p-Cymene	148	6330	0.808	0.270	3.56
69	p-Cymene	151	6460	0.825	0.278	3.67

Material Balances.— In an effort to determine the amount of reacting pinene accounted for in maleic acid, formaldehyde and CO_2, carbon balances were calculated for several runs. The results are summarized in Table XXVII.

Table XXVII. Carbon Balances.

Run No.	Compound Oxidized	Carbon In Feed Mols	Carbon Maleic Acid Mols	Carbon In Formaldehyde Mols	Carbon In CO_2 Mols	Total Carbon Accounted For	
						Mols	%
64	Pinene	0.607	0.0676	0.0398	0.236	0.343	56.6
65	Pinene	0.827	0.0928	0.0527	0.332	0.478	57.8
66	Dipentene	0.515	0.0559	0.0382	0.200	0.294	57.1
67	Dipentene	0.412	0.0444	0.0309	0.172	0.247	60.0
68	p-Cymene	0.474	0.0511	0.0385	0.169	0.258	54.4
69	p-Cymene	0.392	0.0436	0.0325	0.144	0.220	56.1

It is evident that only 55-60 % of the reacting hydrocarbon has been accounted for. S ome of the remainder went to form the resinous deposit that collected on the walls of the reactor exit. An additional amount was converted to color bodies which were present in the product in amounts sufficient to cause trouble in the titrations. In addition, all the aldehyde is reported as formaldehyde, although the analytical method which was used did not distinguish between the various classes of aldehydes. The presence of toluic aldehyde was established by qualitative tests, and if this were determined separately the carbon balance would be improved somewhat as a result of the much greater carbon content of this aldehyde.

Life of the Catalyst.— In order to determine whether or not the activity of the catalyst had diminished during use, a final run was made duplicating one carried out shortly after the catalyst was prepared. During the interval between these two runs a total of 652 grams of hydrocarbon was converted by a c atalyst containing 2.5 grams of V_2O_5. The active material therefore had converted 275 times its weight of hydrocarbon. The data in Table XXVIII indicate that the activity of the catalyst remained practic ally constant during this interval. Weiss and Downs (79), on the basis of their experience with V_2O_5 as a catalyst for the commercial production of phthalic anhydride, concluded that this catalyst will convert about 20,000 times its weight of hydrocarbon before its activity begins to decline. Evidently the catalyst used in this investigation should convert about 46 kg. of pinene before this effect becomes noticeable. It is possible that in laboratory work, in which highly purified materials are

used, the life of the catalyst may be much longer.

Table XXVIII. Test of Catalyst Life.

Run No.	O_2-Pinene Ratio	Space Velocity l/hr.	Contact Time Sec.	Temp. °C.	Yield %
14	27.8	4020	0.20	464	20.3
71	28.0	3924	0.20	464	20.0

SUMMARY

1. An apparatus suitable for carrying out the vapor phase catalytic oxidation of volatile organic liquids has been described.

2. The operation of the apparatus, as applied to the production of maleic acid from pinene, has been described in detail.

3. Methods of analysis of the pinene oxidation product for maleic acid, formaldehyde and CO_2 have been given.

4. Using a V_2O_5 catalyst, maleic acid was found to be the only acid formed in appreciable quantity. The optimum conditions for its formation were determined and were found to be:

Temperature	425°C.
Space Velocity	6500 l/hr.
Mol Ratio of Oxygen to Pinene	100
Maximum Yield Obtained	29.5 %

5. Formaldehyde was shown to be the principal aldehyde formed in the oxidation of pinene, dipent ene and p-cymene. Traces of toluic aldehyde were shown to be present.

6. Pinene, dipentene and p-cymene were found to give the same yields of maleic acid, formaldehyde and CO_2, when oxidized under similar conditions.

7. Material balances were calculated on the basis of the maleic acid,

formaldehyde and CO_2 formed in the oxidation of pinene, dipentene and p-cymene. They showed that these three products account for 55 - 60 % of the hydrocarbon reacting.

8. It may be concluded on the basis of this study that further research, with the object of improving the yield of maleic acid, is necessary before the process could be applied commercially. Further work also is indicated in order to discover the products of the reaction other than maleic acid, formaldehyde and CO $_2$, so that the reacting material may be more completely accounted for.

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BIOGRAPHICAL ITEMS

Charles Kittredge Clark was born at Berkeley, California, on October 15, 1906, and received his early education in the public schools of that city. He attended S tanford University and received the degree of Bachelor of Arts in Chemistry in 1928 and the degree of Engineer in Chemistry in 1929. Before coming to the University of Florida in 1937, he served for two years as Research Chemist at the Hercules Powder Company, Wilmington, Delaware; for one year as Research Chemist at the Shell Development Company, Emeryville, California; and for five years as Research Chemist at the Naval Stores Station of the United States Department of Agriculture at Lake City, Florida. He is a member of the Society of Sigma Xi and of the American Chemical Society.

This dissertation was prepared under the direction of the Chairman of the candidate s Supervisory Committee, and has been approved bt all members of the committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

Date August 24, 1940

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